Proceedings of the EURL-FCM training workshop 2015 "Science collaborations behind safety in innovation for FCM"

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Ispra

C. Simoneau (ed)

2015

Joint Research Centre

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Abstract

The JRC organised a workshop for the network of National Reference Laboratories to provide the latest state of the art look at "science behind innovation and safety for food contact materials".

Invited presentations were selected to represent relevant forward looking recent or on-going research projects at national or regional levels with a focus on collaborations across institutions and with industries. These included a short review on advances for food contact from RTD projects, a briefing on a Marie Curie Project dedicated to the safety in Use and emerging technologies in food packaging pathways (Safemtech) a National Project dedicated to the design of barrier and systems (SafeFoodPack Design), a Research project from a collaboration from professional Association and a national institute on migration testing and modelling of nanoparticles from nano-polymer-composites, a national project on lowering energy and contaminants in bread and rusk tins, an inter-industry project by professional associations on developing migration testing guidelines for non-harmonised areas, and a professional association funded FCM "matrix" exposure tool for public use.

The event promoted better access to information and fostered the use of state of the art progress in innovative applied research to open up practical ideas and networking contacts for future.

1. Introduction

Food availability, abundance and safety are paramount to feed the growing world population. Packaging protects food against microbiological /chemical contaminations, bioterrorism and product tampering, it is a physical support to information (ensuring traceability in the food chain), and is the key to achieve long lasting quality and shelf life of foods. Innovation is therefore a major driver. Yet, while new materials and technologies are constantly being developed, these must also be safe.

The JRC organised a workshop for the network of National Reference Laboratories to provide the latest state of the art look at science behind innovation and safety for food contact materials. Invited presentations were selected to represent relevant forward looking recent or on-going research projects at national or regional levels with a focus on collaborations across institutions and with industries. The event aimed to promote access to information and foster the use of state of the art progress in innovative applied research to open up practical ideas and networking contacts for future.

The presentations are reported in the next sections together with the agenda of the day.

2. Agenda

09:00-09:15 Arrival at the Joint Research Centre // Welcome // Welcome coffee //

09:20-09:50 A look back to advances from RTD for food contact

C. Simoneau, JRC

09:55-10:25 Safemtech: Safety in Use and Emerging Technologies in Food Packaging Pathways (IAPP) 2010-2014

Dr. Jesús Salafranca, University of Zaragoza Spain

10:30-11:00 Coffee break

11:00-11:30 SafeFoodPack Design: design of barrier and systems

Dr. Olivier Vitrac, INRA Agroparistech, Paris France

11:35-12:05 Migration testing and modeling of nanoparticles from nano-polymer-composites. A collaboration with Plastic Europe, the European Carbon Black Association and from the European Silica producer association

Dr. Angela Stoermer, IVV Fraunhofer institute, Freising, Germany

12:10-12:40 SAFE bread TIN: lowering energy and contaminants in bread and rusk tins

Dr. Ronan Cariou, ONIRIS, Nantes, France

12:40-13:00 Q&A

13:00-14:30 Lunch / Buffet

14:30-15:00 Migration testing guidelines- a professional association initiative for the non harmonised areas

Peter Oldring, Facet Industry group

15:05-15:35 Matrix exposure tool for public use

Dario Dainelli, EUPC / Matrix group

16:10-17:00 Q&A and end of meeting

3. Presentations

A look back to advances from RTD for food contact – Dr Catherine Simoneau, European Commission Joint Research Centre, Ispra, Italy

A world of man made materials

Conventional :

- Plastics, including multilayers
- Regenerated cellulose, Paper and board,
- Glass and ceramics,
- Elastomers, Metals, Wood, textile, waxes etc.

FCM is a technologically driven sector

These bottles are 30% plant based (sugar cane)- in operation since 2011 in DK
Source: http://www.beveragedaily.com

Biobased plastics for yoghurt: use 43% less fossil resources compared to the polystyrene containers
Source: http://www.sustainablebrands.com

PET: FCM PET is recycled for food and non food uses: In 2011 39% rPET in the EU into fibres, 25% into pack containers.
Source: http://www.petcore-europe.org/

Sustainable: do more with less!

- Biobased: made from renewable sources
- Recycled: PET recycling including for FCM

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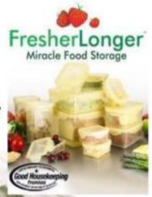
Innovative materials??



Antibacterial bags and boxes

Active materials:
acts on atmosphere inside package
- Antibacterial, antioxidant etc

nanoTitatium filter, antibacterial, anti odour (deo), trap for dust particles

Intelligent:
follow quality during shelf life
- indicators of temperature.
- Freshness/spoilage
- integrity /leakage

Including nano

tracking

protect beer from "UV burn"

Protecting juices against light that damages vitamins

A number of regulatory frameworks..

Functionality
- Handle & protect
- Advertise and inform (labelling)

Product Safety

- General Safety
- Liability

Environment
- Waste
- Sustainability

Food Safety
- Food law
- Food contact legislation
- Food Official Controls

Importance of the consumer's voice

Package — **INTERACTION** — **Foods**

ACCEPTABILITY OF PACKED FOOD
By the consumer

Success in innovation means safety by design…

ASPECTS OF FOOD SAFETY

- **Ensure chemical safety**
- **Provide for regulatory compliance**

European Commission

Innovations means science behind

- http://cordis.europa.eu/home_en.html
- Large EU investments in research via Framework programmes
  - FP 5
  - FP6
  - FP7
  - Horizon 2020

- Other RTD tools – Cost, Marie Curie etc

- National projects

⇒ Many research projects multipartners have led to innovative concepts, and some to anticipate developments for harmonised legislative options….

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European Commission

Examples of FP7 projects

NANOPACK- ICT 216176	Nano packaging technology for interconnect and heat dissipation (2007-2010)
FACET-KBBE 211686	Flavours, additives and food contact material exposure task (2008-2012)
NAFISPACK-KBBE 212544	Natural antimicrobials for innovative and safe packaging (2008-2011)
PERFOOD-KBBE – 227525	PERFluorinated Organics in Our Diet"Perfluorinated Organic Compounds in the Foodchain: a Risk Analysis to Support Government Policy"
FLEXPAKRENEW-NMP 207810	Design and development of an innovative ecoefficient low-substrate flexible paper packaging from renewable resources to replace petroleum based barrier films
REBIOFOAM-NMP 214425	Development of a flexible and energy-efficient pressurised microwave heating process to produce 3D-shaped renewable bio-polymer foams for a novel generation of transportation packaging
NANOPACK-PEOPLE 223832	Multifunctional nanomaterials for intelligent food packaging applications (2008-2012)
SAFETECHNOPACK-REGIONAL 202772	Improving the scientific and technological research capacity of food institute on safety and technology of food packaging (2008-2011)
COBAPACK-SME 231106	Development of a new recyclable long life co-injected high barrier packaging for food applications, with broad design possibilities and reduced manufacturing costs (SME)
RPET-FC-SME 232055	Environmentally friendly food packaging tray with lower carbon footprint (2009-2011)
HORTIBIOPACK-SME	Development of innovative biodegradable packaging system to improve shelf life, quality and safety of high-value sensitive horticultural fresh produce (2009-2011)
FRESHFILM-SME 232217	New active recyclable packaging with natural antioxidising for the extension of the fresh food shelf live (2009-2011)
BREW-PACK-SME 232216	Multi-layer biopolymer films demonstrating selective gas barrier and functional properties suitable for high performance food packaging, derived from integrated bio-refining of sustainable biomass (2009-2011)
BIOSURF-SME 232172	Development and implementation of a contact biocide polymer for its application as antimicrobial and anti-deposit surfaces in the food industry (2009-2011)

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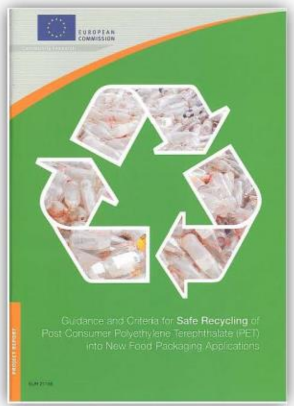
Example of FP6 projects

SAFE FOOD	through a New Integrated Risk Analysis Approach for Foods
MIGROSURE	migration of chemicals from packaging toward foods.
PERFORCE	Activity New and Emerging Science and Technology
HIGHQ RTE-FOOD 23140	Innovative non-thermal processing technologies to improve the quality and safety of ready-to-eat (RTE) meals
NOVELQ-FOOD 15710	Novel Processing Methods for the Production and Distribution of High-Quality and Safe Foods (2006-2011)
ANTIOXIPACK-FP6-MOBILITY 24183	The design of active packaging for food applications with oxygen scavenging or antioxidant capacity (2005-2007)
MICRO-GMAP-FP6-MOBILITY 42609	Multipurpose tuneable microwave plasma source of germicidal modified atmospheric packaging for food industries (2006-2009)
SUSTAINPACK-FP6-NMP 500311	Innovation and Sustainable Development in the Fibre Based Packaging Value Chain (2004-2008)
POLYCOAT-FP6-NMP 505635	Economical exploitation of polymer coated steel sheet in large-scale production of new can types by the European can industry (2004-2006)
PICUS-FP6-SME 17684	Development of a 100 % Biodegradable Plastic Fiber to Manufacture Twines to Stake Creeping Plants and Nets for Packaging Agricultural Products (2005-2007)
MIGRESIVES-FP6-SME 30309	Research programme on migration from adhesives in food packaging materials in support of European legislation and standardisation (2007-2010)
WHEYLAYER-FP6-SME 218340	Whey protein-coated plastic films to replace expensive polymers and increase recyclability (2008-2011)
ONLINE TRACEABILITY-FP6-SME- 32947	Online quality control and traceability for the food processing industry
FOOD PRO - FP6-SME 508374	Ohmic heating for food processing (FOOD PRO) (2004-2006)
SAFEFILL - FP6-SME 32685	Safe aseptic flexible efficient filling of liquids (2006-2008)

RTD projects in anticipation of legislation

FP5 EU TRD "Recyclability":

- Research on recycling of PET plastics (what contaminants can be eliminated or brought by recycling)
  - ⇒ RTD technical guidance
  - ⇒ Peer reviewed publications => acceptance
- Led to a legislation on recycling
- EFSA process for authorisation



Active packaging

- Several research projects (actipack, nafispack etc)
- Many publications with sound data
- Confidence on which to develop a harmonised legislation
- Now also EFSA process for authorisation

Bio materials, Paper and board, adhesives, nanomaterials

What has science data given to compliance?

Cannot test on every food: development of "simulants"

Liquids simulating different types of foods (acidic, alcoholic, fatty, dry)- e.g. oil for fatty foods

⇒ new inception of Tenax as simulant for dry foods was based on > 10 years research in both academia and in EU projects

⇒ Change of milk simulant from 10% to 50% also based on large kinetics within EU project (migrosure, FACET)

⇒ Extensions from packaging to kitchenware (at the crossroads of legal principles, pragmatic science and consumer behaviour)

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Sound data to support compliance testing

Need to simulate the shelf life

- Exposure of the material to time/ temperature (worst) conditions (with simulants)

Migration – predictable..

- ***D_P - diffusion coefficient***
- ***$K_{P,F}$ - partition coefficient***

- **Faster! modelling**

⇒ development of diffusion modelling also the results of ***SMT project 1997-2000***

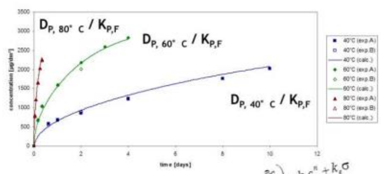
⇒ Taken into peer referred publications

⇒ Acceptance for regulatory purposes and authorisation

  ⇒ Taken into practical guide -→ now in note for guidance

  ⇒ Recognised for PE, PP, PS, PET, PA

  ⇒ Now also for more complex systems multilayers, real foods



$$-\left|\frac{\partial c}{\partial t}\right|_{total} = -D\left(\frac{\partial^2 c}{\partial x^2}+\frac{\partial^2 c}{\partial y^2}+\frac{\partial^2 c}{\partial z^2}\right)+\left(v_x\frac{\partial c}{\partial x}+v_y\frac{\partial c}{\partial y}+v_z\frac{\partial c}{\partial z}\right)+k_r c^n+k_s\sigma$$

$$\frac{\partial c}{\partial t} = D\cdot\frac{\partial^2 c}{\partial x^2}$$

- **Better: mimic long storage conditions**

⇒ now the use of an Arrhenius equation into legislation

t2 = t1 * Exp ((-Ea/R) * (1/T1-1/T2))

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Estimation of exposure

Predicting migration

Estimate EU consumer exposure to Food Contact Material Substances

RTD project FACET 2008-2012 and its sustainability

A path towards better exposure assessment

FP6 Food migrosure + FP7 FACET: a new exposure tool

- Research on kinetics of migration from plastics into real food
- Research on assessment of additives flavourings and food contact materials
- Now a software output (JRC entity towards sustainability)
- Tested in an EFSA assessment

FACET can estimate

- *exposure to existing substances in FCMs at varying levels of sophistication*
- *exposure for substances in foods measured in surveillance surveys*
- *exposure to (new or existing) substances from new packaging*
- *exposure to new substances* ***and NIAS***

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Ensuring safety in innovation based on "science with a purpose"

Consumer
Demands convenience, quality, protection

Industry
Innovation - (functional, safe, smart/intelligent, sustainable), compliant in a global market

Consumer groups, media
Acceptance, public perception

European Food Safety Authority
Risk assessment

DG SANCO Member State Competent authorities
Risk Management, EU harmonisation

Official Controls
Enforcement compliance

CEN/ISO
Standardisation

Council of Europe
Input in non-harmonised areas

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Safemtech: Safety in Use and Emerging Technologies in Food Packaging Pathways (IAPP) 2010-2014 - Dr. Jesús Salafranca, University of Zaragoza Spain


UNIZAR & GOGLIO
2
GUIA
instituto de investigación en ingeniería de Aragón
Universidad de Zaragoza
GOGLIO
Head: Prof. Dr. Cristina Nerín
Head: Dr. Osvaldo Bosetti
experience
Analytical chemistry
Food Packaging Interactions
Diffusion and migration of adhesives in food packaging
Packaging materials & materials science & technology
Active food packaging
Microbiological performance
Intelligent food packaging
Chemical sensors
TOK
Food packaging production
Design of packaging
Packaging materials & materials science & technology
Adhesive formulations
Printing inks
Engineering
Production of laminates
multidisciplinarity
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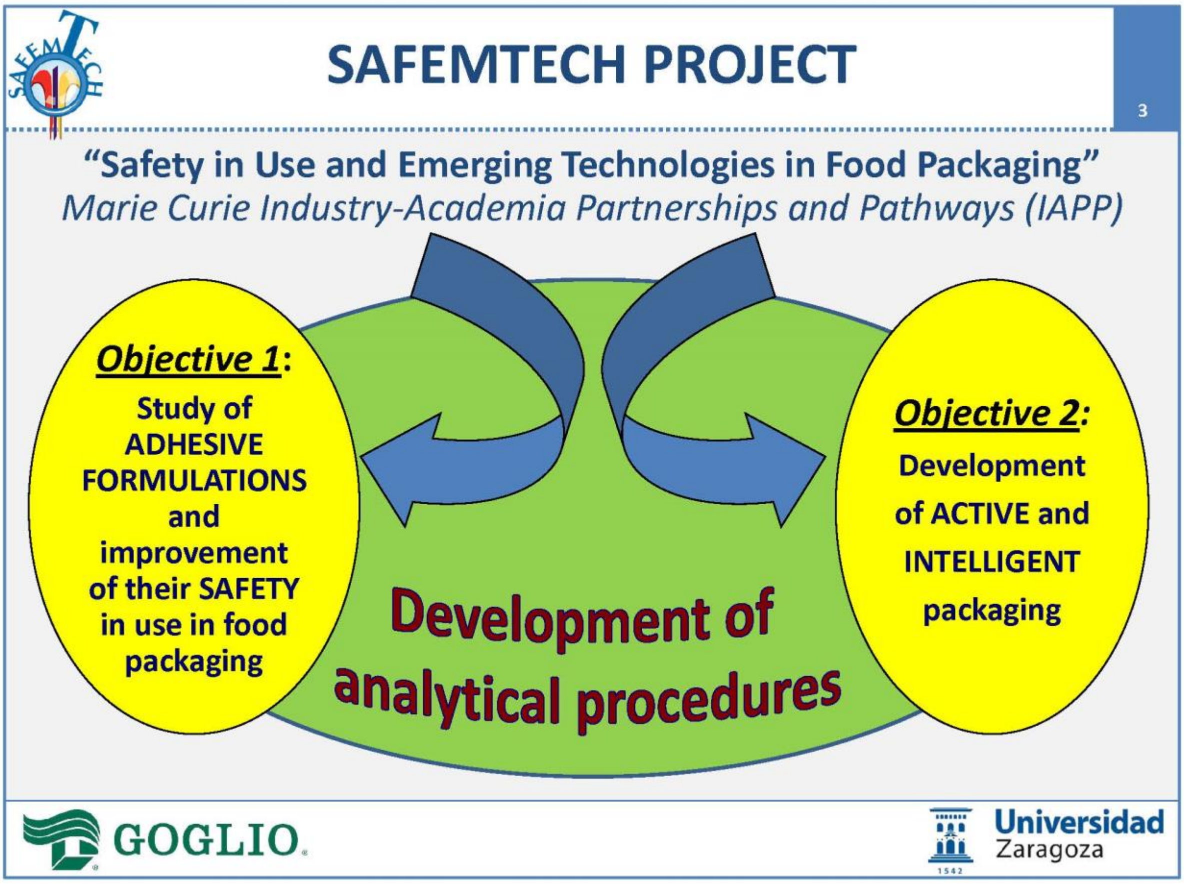
SAFEMTECH PROJECT
3
"Safety in Use and Emerging Technologies in Food Packaging"
Marie Curie Industry-Academia Partnerships and Pathways (IAPP)
Objective 1:
Study of ADHESIVE FORMULATIONS and improvement of their SAFETY in use in food packaging
Objective 2:
Development of ACTIVE and INTELLIGENT packaging
Development of analytical procedures
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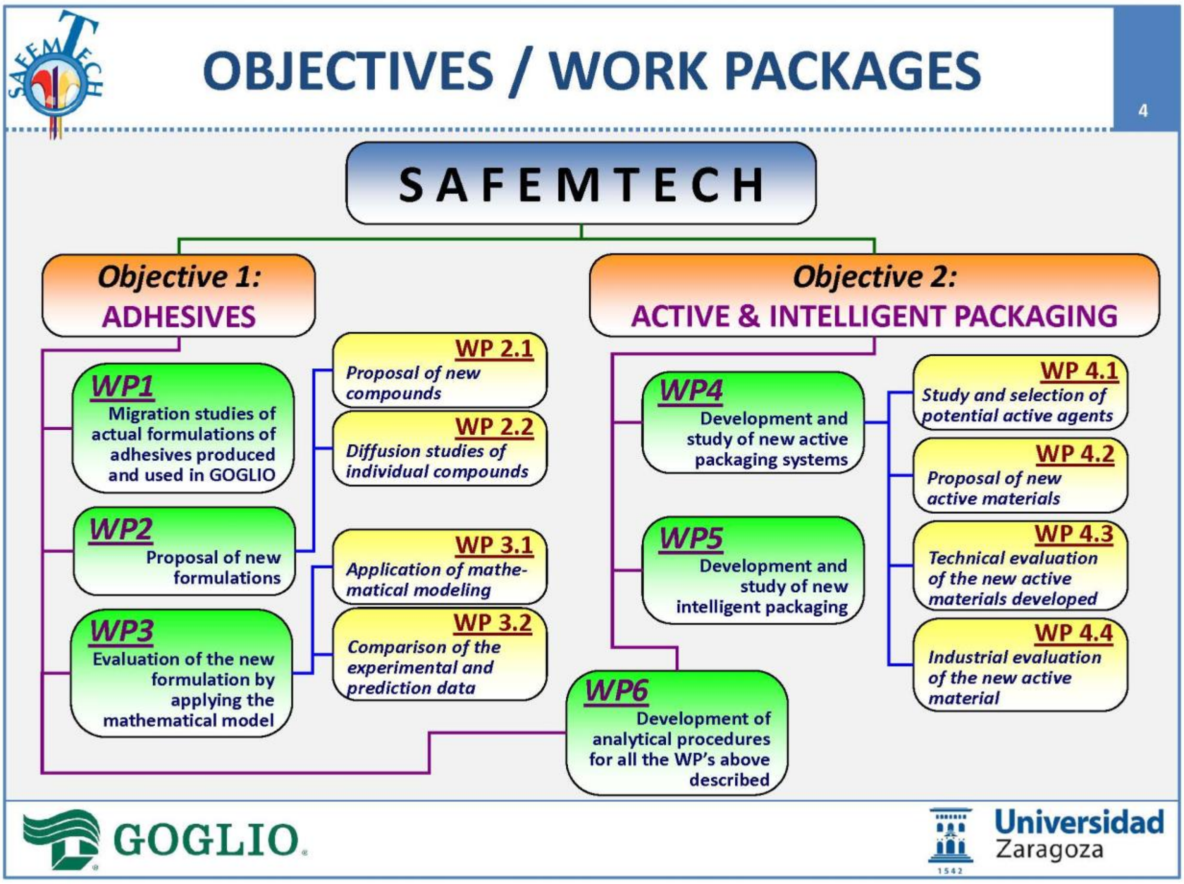
OBJECTIVES / WORK PACKAGES
4
SAFEMTECH
Objective 1:
ADHESIVES
Objective 2:
ACTIVE & INTELLIGENT PACKAGING
WP1
Migration studies of actual formulations of adhesives produced and used in GOGLIO
WP2
Proposal of new formulations
WP3
Evaluation of the new formulation by applying the mathematical model
WP 2.1
Proposal of new compounds
WP 2.2
Diffusion studies of individual compounds
WP 3.1
Application of mathematical modeling
WP 3.2
Comparison of the experimental and prediction data
WP4
Development and study of new active packaging systems
WP5
Development and study of new intelligent packaging
WP 4.1
Study and selection of potential active agents
WP 4.2
Proposal of new active materials
WP 4.3
Technical evaluation of the new active materials developed
WP 4.4
Industrial evaluation of the new active material
WP6
Development of analytical procedures for all the WP's above described
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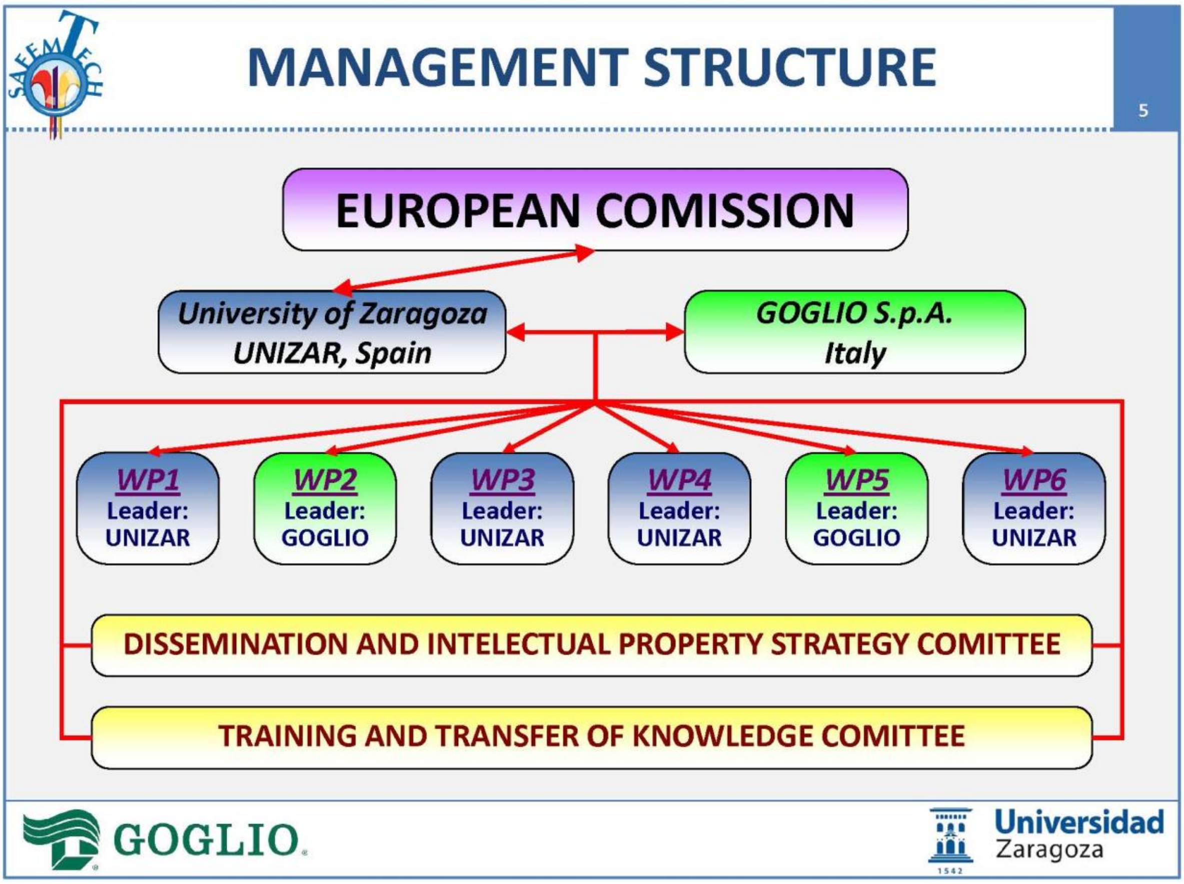
MANAGEMENT STRUCTURE
5
EUROPEAN COMISSION
University of Zaragoza
UNIZAR, Spain
GOGLIO S.p.A.
Italy
WP1
Leader:
UNIZAR
WP2
Leader:
GOGLIO
WP3
Leader:
UNIZAR
WP4
Leader:
UNIZAR
WP5
Leader:
GOGLIO
WP6
Leader:
UNIZAR
DISSEMINATION AND INTELECTUAL PROPERTY STRATEGY COMITTEE
TRAINING AND TRANSFER OF KNOWLEDGE COMITTEE
GOGLIO
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DELIVERABLES

6

Deliverables	Initial
D 1.1	Migrants identified from actual adhesives
D 1.2	Migration values from actual adhesives
D 2.1	Proposal of new compounds as components of the new formulations
D 2.2	Diffusion values for the new compounds
D 3.1	Prediction of migration by mathematical model
D 3.2	Comparison of data and validation of the model
D 3.3	Training of GOGLIO technicians about the model for migration prediction
D 4.2.1	Proposal of a new antioxidant active packaging
D 4.2.2	Proposal of a new technology for producing active packaging
D 4.3.1	Antioxidant efficiency of the active agents
D 4.3.2	Antioxidant efficiency of the active packaging materials
D 4.4.1	New active antioxidant materials for industrial use
D 4.4.2	New technology for producing new active materials
D 4.4.3	Proposal of international patent on the new active packaging developed and produced
D 5.1	New intelligent packaging

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IDENTIFICATION OF NIAS

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NIAS = Non Intentionally Added Substances

NIAS are all the compounds that could be

- formed during polymerization as by-products of curing reaction…
- *or* already present into raw material as by-product of their production…
- *or* degradation products.

For all these reasons, NIAS are *unexpected*

RISK ASSESSMENT OF NIAS

- EUROPEAN LEGISLATION (EU 10/2011)
- NATIONAL LEGISLATION
- TOXICITY REPORTS

NO TOXICITY DATA

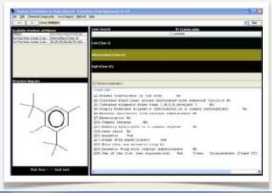
Threshold of Toxicological Concern (TTC) approach

CRAMER RULES

Class I (Low)
< 1.8 mg/person/day

Class II (Intermediate)
< 0.54 mg/person/day

Class III (High)
< 0.09 mg/person/day



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THE BEGINNING: PAA's

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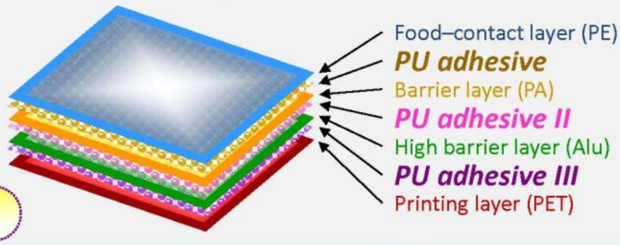
- ***Primary aromatic amines (PAA)*** are products from **residual isocyanates in polyurethane adhesives**, the most used in **multilayer** plastic packaging materials not completely cured

- PAA can be generated from **hydrolysis of polyurethanes** when packaging materials are used in **acidic medium under retorting conditions** (T > 121 °C)



18 MULTILAYERS TESTED

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UHPLC-Q-TOF/MS^E METHOD

9

Main capabilities

- Powerful analytical system
- Exact mass measurement
- Unique molecular structure assignation
- Very complete software MassLynx® with specific modules
- Innovative MS^E: exact mass from precursor ion and daughter fragments in the same run

UHPLC-Q-TOF-MS^E system

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UNEQUIVOCAL IDENTIFICATION OF NIAS

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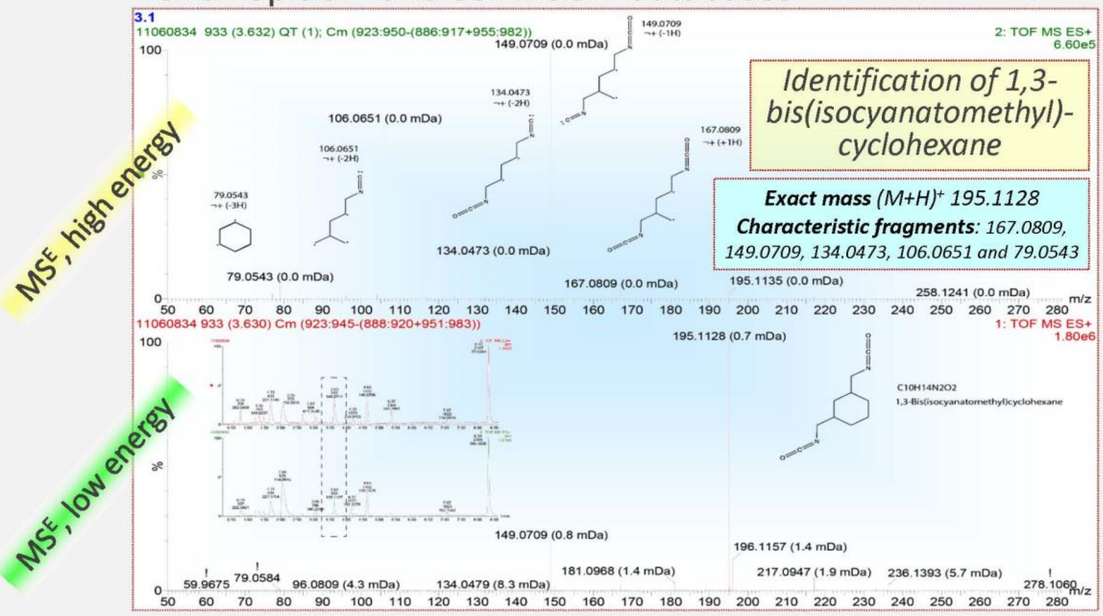
- ChemSpider® and SciFinder® databases



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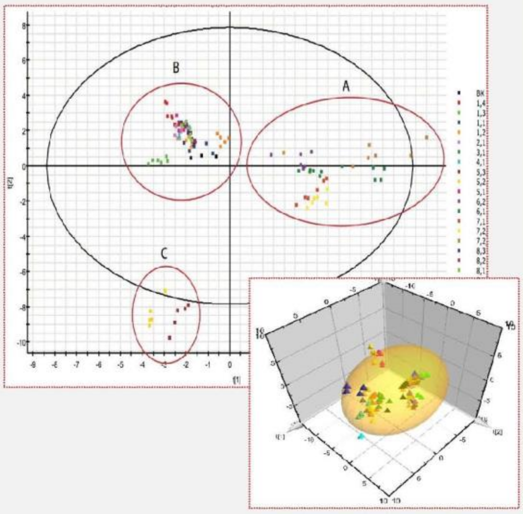
A POWERFUL TOOL: CHEMOMETRICS

11

Pattern recognition (MarkerLynx XS®)

- Principal component analysis (PCA) discovered <u>3 sample groups</u>
  - ✓ **Group A**: OPA + CPP
  - ✓ **Group B**: PE
  - ✓ **Group C**: PE/EVOH



- <u>**PCA differentiated between the kind of material**</u> rather than kind of adhesive
- In other words, the most important **NIAS** seemed to **come from the material itself, not from the adhesive**

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RESULTS FROM NIAS DETERMINATION

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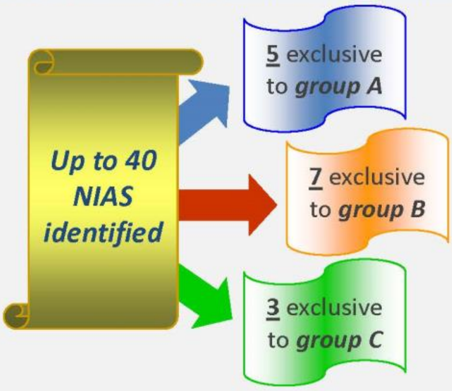

- <u>**MIGRANTS FROM ADHESIVES**</u>**:** Triphenyl phosphate; 1,6-dioxacyclododecane-7,12-dione; unknown adipate
- <u>**OTHER MIGRANTS**</u>**:** **1,4-trioxacyclotridecane-8,13-dione** (*adhesive*); dodecane (*LDPE*); caprolactam (*OPA+CPP*); 2,4-di-tert-butylphenol (*LDPE, PE/EVOH, adhesives*); BHT (*LDPE, adhesives*)
- <u>**All the laminates comply with EU legislation**</u> (total PAA < 10 µg·kg^{-1})

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ACTIONS TAKEN WITH PROBLEMATIC MIGRANTS

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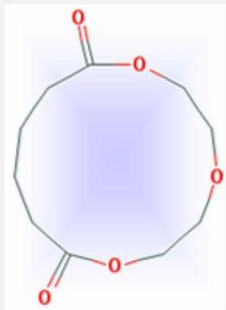
<u>LACTONES</u>

- Found in most of polyurethane adhesives (side-reaction between adipic acid and ethylene glycol)
  - not possible to remove them from the adhesives
  - they migrate very efficiently
  - no experimental data of toxicity available (Cramer class III)
  - not listed in EU 10/2011 (max. migration 10 µg kg^{-1} food)
- <u>SUCCESSFUL ACTIONS</u>
  - ***Higher curing time and temperature***
  - ***Higher thickness of LDPE***
  - ***Incorporation of EVOH as internal layer (functional barrier)***



<u>OTHERS</u>

- Adhesion promoter <u>3-glycidoxypropyltrimethoxysilane</u>: FDA approved but not in Europe. ***Removed from adhesive formulation and substituted*** by 3-aminopropyltriethoxysilane (listed in EU 10/2011)
- One <u>MDI based adhesive</u> with high values of PAA has been ***substituted by a new adhesive with aliphatic HDI*** (risk of formation and migration of PAA completely avoided)

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GAMMA IRRADIATION... WHY?

- ***Gamma radiation*** is one of the safest ways for microbiological decontamination of food packaging materials (aseptic filling)

PROS

- *High penetration capacity (direct use in containers)*
- *Treatment at room temperature and atmospheric pressure*
- *Process parameters versatile*
- *No residues generation*
- *Immediate use of irradiated materials*

CONS

- *Possible undesirable changes in materials (chemical, physical, thermal, mechanical and permeability)*
- *Release of substances present in polymers or generated*
- *Migration processes*

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EXPERIMENTAL

- ***Samples***: thermosealed flexible material bags filled with air / inert gas
- ***Analytical technique***: HS-SPME-GC-MS
- ***13 industrial multilayer packages representative*** of the most usual applications: dry foods, sauces, ready-to-eat meals, hot-filling or aseptic-filling

Sample	*Structure (from outer to inner layer)*
1	PET || ALU || PA || PE
2	PET || ALU || PA || PP
3	PET || ALU || PET || PE
4	PET || ALU || PET || PP
5	PET || PE
6	PET || PETmz || PE
7	PET || PA || PE + PP
8	PET || coexPE–EVOH
9	PET || ALU || PE+PB
10	coexPE–EVOH || PE
11	PE –ALU –PA –PE || PE–PE || PE
12	PE –PETmz –PE || PE–PE || PE
13	LLDPE –PETmz –LLDPE || coexLLDPE–EVOH–LLDPE || LLDPE

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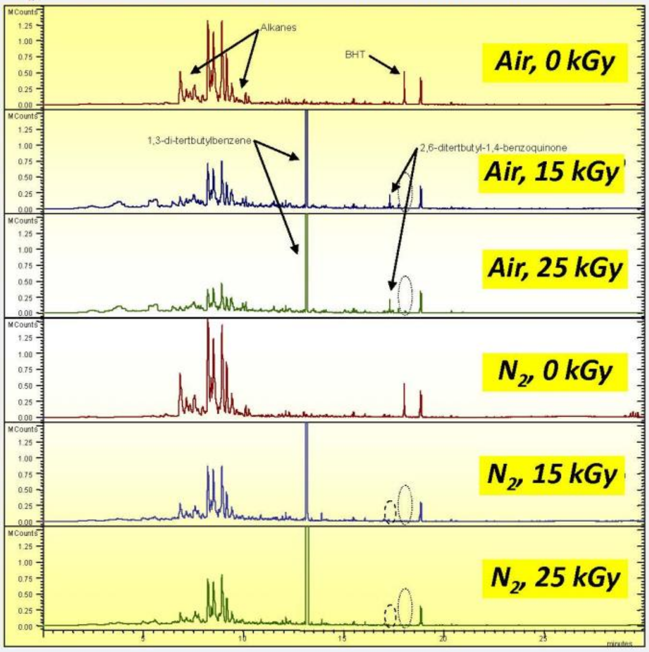
DATA PROCESSING



- ***Antioxidants*** (e.g. BHT) are present in unirradiated materials
- ***Hydrocarbons*** decrease slightly when irradiating
- ***Oxidation compounds*** (e.g. 2,6-ditertbutyl-1,4-benzoquinone) appear as a consequence of gamma irradiation
- ***1,3-ditertbutylbenzene*** is the most representative compound generated in irradiated samples

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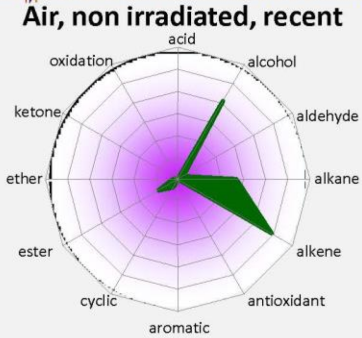
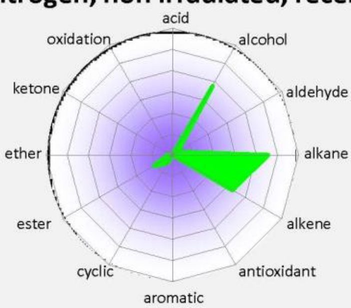
EFFECT OF IRRADIATION AND FILLING GAS

Air, non irradiated, recent



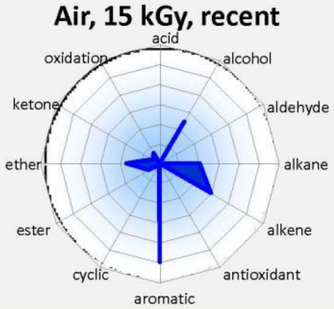
Nitrogen, non irradiated, recent



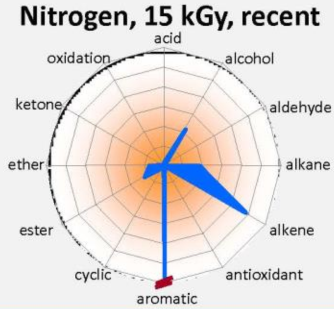
Very similar profiles

Oxidation (air)
Aromatics (> N_2)
Esters (N_2)

Air, 15 kGy, recent



Nitrogen, 15 kGy, recent



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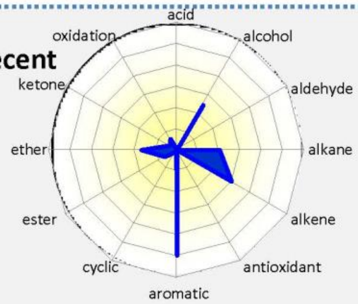
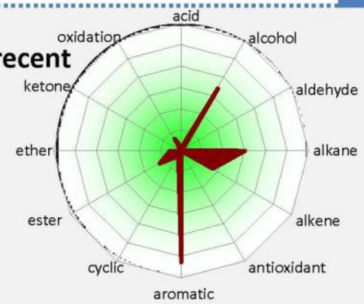
EFFECT OF IRRADIATION DOSE

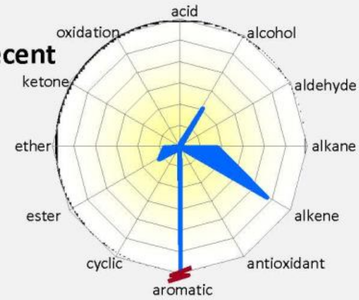
Air, 15 kGy, recent



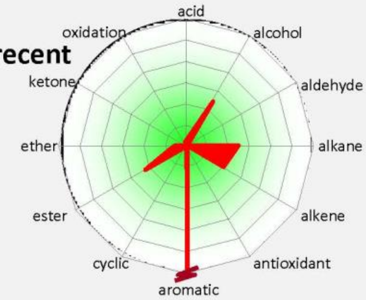
Air, 25 kGy, recent



N_2, 15 kGy, recent



N_2, 25 kGy, recent



Only small differences between 15 and 25 kGy

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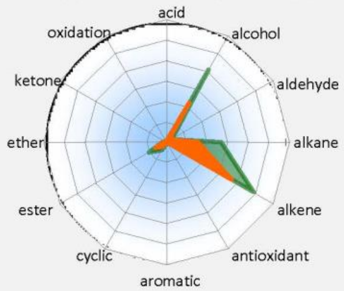
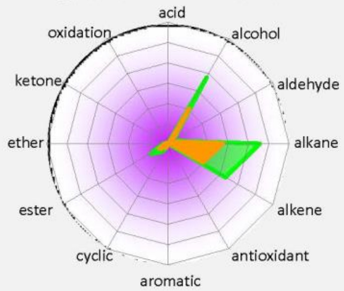
EFFECT OF LONG-TERM STORAGE

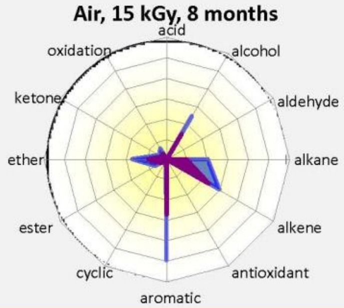
Air, non irradiated, 8 months



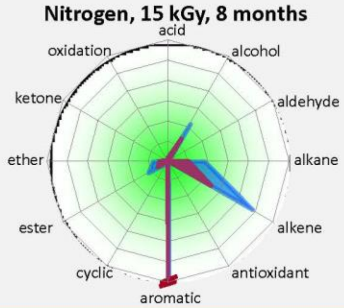
Nitrogen, non irradiated, 8 months



Air, 15 kGy, 8 months



Nitrogen, 15 kGy, 8 months



- ***Profiles almost identical*** between recent and 8-month storage samples
- ***Generalized reduction (~45%)*** of all the compounds
- ***Fast initial release***, then slow reabsorption by the polymeric matrix (***equilibrium***)

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QUANTITATIVE RESULTS ($ng \cdot dm^{-2}$)

20

Sample	acid	alcohol	aldeh.	alkane	alkene	aox	aromatic	cyclic	ester	ether	ketone	oxid.	*Total*
001	0*	63	0*	40	50	3	50	409	120	9	24	7	*775*
015	24	44	11	3	5	0*	1021	47	194	66	98	34	*1547*
032	24	54	15	2	4	0*	1040	48	216	93	124	38	*1658*
047	0*	61	3	47	49	2	43	408	115	7	29	7	*771*
063	2*	15	19	0*	4	0*	1033	23	174	87	47	1	*1405*
094	0*	155	14	195	356	0*	2	92	85	14	7	1	*921*
122	0*	92	1	147	209	0*	179	8	55	95	50	11	*847*
146	1*	113	1	190	106	0*	156	63	95	26	1	20	*772*
170	0*	131	10	302	216	0*	2	99	83	12	8	1	*864*
191	1*	77	1	128	333	0*	310	16	94	40	5	5	*1010*
230	0*	73	0*	50	129	4	44	71	66	5	15	6	*463*
...	...	...	...	...	...	...	...	...	...	...	...	...	*...*

- ***None*** of the ***non-listed substances and NIAS*** identified and quantified ***surpassed the limit of 10*** $\mu g \cdot kg^{-1}$ (equivalent to 1670 $ng \cdot dm^{-2}$) established in Commission Regulation (EU) No 10/2011

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SET-OFF MIGRATION

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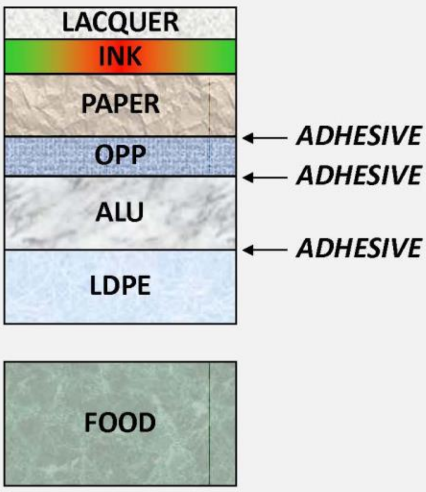
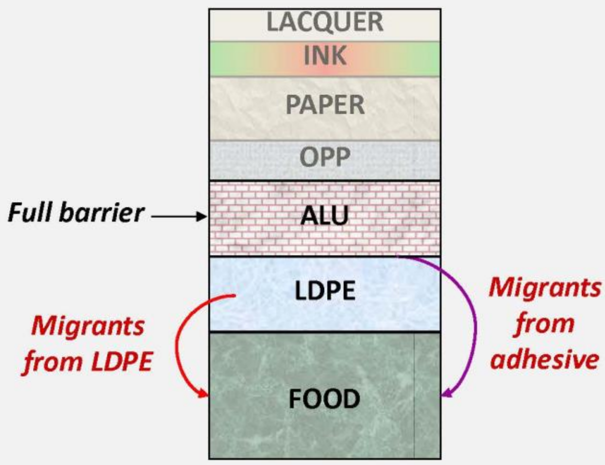
MULTILAYER MATERIAL



CONVENTIONAL MIGRATION



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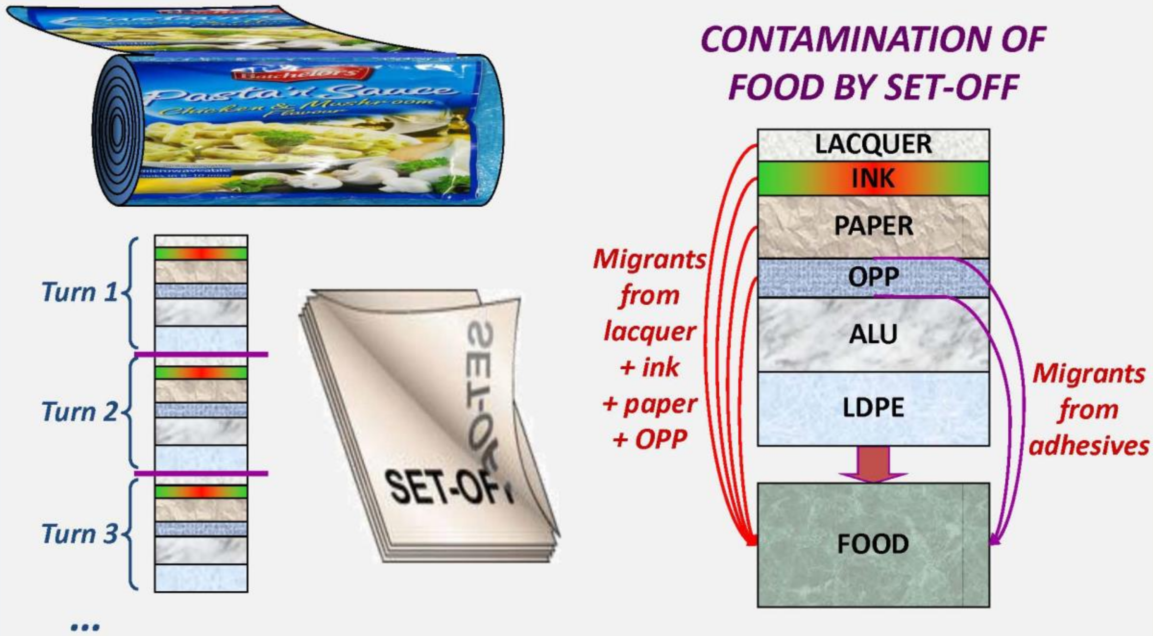
SET-OFF MIGRATION

22



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SET-OFF MIGRANTS FROM INKS (UPLC-Q-TOF)

23

Migrants (RT_mass)	Intens. (1-3)	Adduct	Molecular formula	Candidates	ΔmDa /Δppm	Remarks
4.93_299.1108	2	MNa^+	$C_{12}H_{20}O_7$	Citric acid triethyl ester CAS: 77-93-0	0.3/1.0	Plastizicer in packaging ink
5.63_285.2909	2	MH^+	$C_{17}H_{36}N_2O$	Schercodine CAS: 3179-80-4	0.4/1.4	Emulsifier
5.92_271.1885	1	MNa^+	$C_{13}H_{28}O_4$	Tripropyleneglycol monobutyl ether CAS: 55934-93-5	-0.2/-0.7	Packaging ink solvent
5.96_299.1835	2	MNa^+	$C_{14}H_{28}O_5$	Triethylene glycol caprylate CAS:28397-10-6	0.0/0.0	Surfactant: emulsify, lubricate
6.09_313.3217	2	MH^+	$C_{19}H_{40}N_2O$	Schercodine M/ Myristamidopropyl dimethylamine CAS: 45267-19-4	-0.4/-1.3	Non-ionic surfactants
6.39_343.2965	1	MH^+	$C_{19}H_{38}N_2O_3$	Lauraimidopropyl betaine CAS: 4292-10-8	-0.1/-0.3	Surfactant
6.98_425.2151	2	MNa^+	$C_{20}H_{34}O_8$	Acetyl tributyl citrate CAS: 77-90-7	1.1/2.6	Plastizicer

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SCIENTIFIC PUBLICATIONS

1. *D. Pezo, M. Fedeli, O. Bosetti, C. Nerín.* Aromatic amines from polyurethane adhesives in food packaging: The challenge of identification and pattern recognition using Quadrupole-Time of Flight-Mass Spectrometry[E]. *Analytica Chimica Acta, 756 (2012), 49–59.*

2. *J.S. Félix, F. Isella, O. Bosetti, C. Nerín.* Analytical tools for identification of non-intentionally added substances (NIAS) coming from polyurethane adhesives in multilayer packaging materials and their migration into food simulants. *Analytical and Bioanalytical Chemistry 403 (2012) 2869–2882.*

3. *F. Isella, E. Canellas, O. Bosetti, C. Nerín.* Migration of non intentionally added substances from adhesives by UPLC–Q-TOF/MS and the role of EVOH to avoid migration in multilayer packaging materials. *Journal of Mass Spectrometry 48 (2013) 430–437.*

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SCIENTIFIC PUBLICATIONS

4. *D. Carrizo, G. Gullo, O. Bosetti, C. Nerín.* Development of an active food packaging system with antioxidant properties based on green tea extract. *Food Additives & Contaminants: Part A 31 (2014) 364–373.*

5. *M. Aznar, C. Domeño, C. Nerín, O. Bosetti.* Set-off of non volatile compounds from printing inks in food packaging materials and the role of lacquers to avoid migration. *Dyes and Pigments 114 (2015) 85–92.*

6. *J. Salafranca, I. Clemente, F. Isella, C. Nerín, O. Bosetti.* Influence of oxygen and long term storage on the profile of volatile compounds released from polymeric multilayer food contact materials sterilized by gamma irradiation. *Analytica Chimica Acta 878 (2015) 118–130.*

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SCIENTIFIC PUBLICATIONS

26

7. Partition, diffusion and migration of 1,4,7-triaxocyclotridecane-8,13-dione, a non-intentionally added compound, from polyurethane adhesives in multilayer food packaging and the barrier effect of EVOH. *Packaging Technology and Science (2015) *Under review*.*
8. Development of an innovative multilayer antimicrobial packaging material for tomato sauce *Food Control (2015) *Under review*.*
9. Extension of shelf life of two fatty foods using an active antioxidant multilayer packaging system containing green tea extract. *Food Control (2015) *Under review*.*

10. Set-off of volatile compounds in multilayer food packaging and specific migration *(2015) *In preparation*.*
11. Migration from printing inks in multilayer packaging materials by GC-MS analysis and pattern recognition with chemometrics. *(2015) *In preparation*.*

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DISSEMINATION ACTIVITIES

27

Several scientific presentations were done during the Project to disseminate the results of SAFEMTECH. Relevant information is available in the website (***http://www.safemtech.eu/***)

- ***SPECIFIC SEMINAR*** *"Adhesives: how could they affect food packaging safety?"* organized in Varese (Italy) during the second year of the project. 9 talks were presented, with 138 attendees from the industry outside the Project.

- ***CLOSING CONFERENCE*** organized in Zaragoza (Spain) at the end of the project. 10 talks were given, with more than 60 attendees present, most of them from the industrial sector.

Hispack 2015

- Recently, two conferences to disseminate the success and results of SAFEMTECH project were given in ***HISPACK 2015***:
  - O. Bosetti: *"TRADEIT Brokerage Event of Packaging"*
  - C. Nerín: *"Migración de adhesivos y su aplicación a film multicapa: proyecto SAFEMTECH"*

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DISSEMINATION ACTIVITIES

28

- D. Pezo, M. Fedeli, O. Bosetti, C. Nerín *"Determinación de aminas alifáticas y aromáticas e identificación de otros migrantes de films multicapas para alimentos por Q-TOF MASAS^E"*. 13as Jornadas de Análisis Instrumental. November 2011, Barcelona, Spain.

- J.S. Félix, F. Isella, O. Bosetti, C. Nerín *"Analytical tools for identification of non intentionally added substances (NIAS) coming from polyurethane adhesives in multilayer packaging materials and their migration into food simulants"*. 5th International Symposium on Recent Advanced in Food Analysis (RAFA). November 2011, Prague, Czech Republic.

- A. Maccagnan, D. Carrizo, J. Félix, O. Bosetti, C. Nerín *"Multi-analysis of 1,4,7-triaxocyclotridecane-8,13-dione in polyurethane adhesive used in multilayer food packaging"*. 26th Symposium on Packaging IAPRI. June 2013, Espoo, Finland.

- J. Salafranca, F. Isella, O. Bosetti, C. Nerín *"Migration of volatile NIAS from food packaging multilayer materials". FIRST AWARD TO POSTER PRESENTATIONS.* Swiss Food Science Meeting. June 2013, Neuchâtel, Switzerland.

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DISSEMINATION ACTIVITIES

29

- C. Nerín, M. Aznar, P. Alfaro *"UPLC-MS-QTOF as a tool for identifying non volatile NIAS from food packaging materials"*. Swiss Food Science Meeting. June 2013, Neuchâtel, Switzerland.

- C. Nerín *"Natural antioxidants anchored on packaging to increase the shelf life. A different perspective"*. SLIM 2014, June 2014, Brunswickm, USA.

- C. Nerín *"The new challenges of food packaging materials"*. The 2nd International Conference of Packaging Technology and Science & The 2nd Asian Packaging Network Conference. October 2014, Wuxi, China.

- C. Nerín *"Discover the latest innovations in active packaging to keep your cakes fresh longer"*. The cake freshness seminar organized by Puratos. March 2015, Brussels, Belgium.

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PATENT: NEW ACTIVE PACKAGING

- New green tea-based antioxidant material developed and patented
- All the requirements fulfilled
- Production at industrial level by GOGLIO
- The material is already in the market

WO2014170426 (A1)

"MULTILAYER ASSEMBLY"

(12) INTERNATIONAL APPLICATION PUBLISHED UNDER THE PATENT COOPERATION TREATY (PCT)

(19) World Intellectual Property Organization
International Bureau

(43) International Publication Date
23 October 2014 (23.10.2014)

WIPO | PCT

(10) International Publication Number
WO 2014/170426 A1

(51) **International Patent Classification**:
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(21) **International Application Number**: PCT/EP2014/057882

(22) **International Filing Date**: 17 April 2014 (17.04.2014)

(25) **Filing Language**: English

(26) **Publication Language**: English

(30) **Priority Data**:
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MI2013A000623 17 April 2013 (17.04.2013) IT

(71) **Applicant**: **GOGLIO S.P.A.** [IT/IT]; Via A. Solari 10, I-20144 Milan (MI) (IT).

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(74) **Agents**: **PONTIROLI, Alessandro** et al.; Piazza San Babila 5, I-20122 Milan MI (IT).

(81) **Designated States** *(unless otherwise indicated, for every kind of national protection available)*: AE, AG, AL, AM, AO, AT, AU, AZ, BA, BB, BG, BH, BN, BR, BW, BY, BZ, CA, CH, CL, CN, CO, CR, CU, CZ, DE, DK, DM, DO, DZ, EC, EE, EG, ES, FI, GB, GD, GE, GH, GM, GT, HN, HR, HU, ID, IL, IN, IR, IS, JP, KE, KG, KN, KP, KR, KZ, LA, LC, LK, LR, LS, LT, LU, LY, MA, MD, ME, MG, MK, MN, MW, MX, MY, MZ, NA, NG, NI, NO, NZ, OM, PA, PE, PG, PH, PL, PT, QA, RO, RS, RU, RW, SA, SC, SD, SE, SG, SK, SL, SM, ST, SV, SY, TH, TJ, TM, TN, TR, TT, TZ, UA, UG, US, UZ, VC, VN, ZA, ZM, ZW.

(84) **Designated States** *(unless otherwise indicated, for every kind of regional protection available)*: ARIPO (BW, GH, GM, KE, LR, LS, MW, MZ, NA, RW, SD, SL, SZ, TZ, UG, ZM, ZW), Eurasian (AM, AZ, BY, KG, KZ, RU, TJ, TM), European (AL, AT, BE, BG, CH, CY, CZ, DE, DK, EE, ES, FI, FR, GB, GR, HR, HU, IE, IS, IT, LT, LU, LV, MC, MK, MT, NL, NO, PL, PT, RO, RS, SE, SI, SK, SM, TR), OAPI (BF, BJ, CF, CG, CI, CM, GA, GN, GQ, GW, KM, ML, MR, NE, SN, TD, TG).

Declarations under Rule 4.17:
— *of inventorship (Rule 4.17(iv))*

Published:
— *with international search report (Art. 21(3))*

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Thank you!

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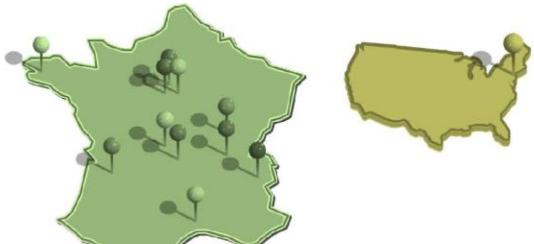
SafeFoodPack Design: design of barrier and systems - Dr. Olivier Vitrac, INRA Agroparistech, Paris France

KEY FIGURES

- Project funded by the French National Research Agency (ANR)
- Reference: ANR_ALIA_009
- **Jan 1st 2011 – Dec 31th 2014**
- 11 partners
- Budget: 2.8 M€
- Grant: 790 k€
- 3 PhDs
- 3 Post-docs
- 1 engineer
- 3 Masters

PROJET FINANCÉ PAR L'ANR - PROJECT FUNDED BY THE ANR



INRA SCIENCE & IMPACT — uB UNIVERSITÉ DE BOURGOGNE — Lyon 1 — ania Association Nationale des Industries Alimentaires — LNE Le progrès, une passion à partager — FRANCE EMBALLAGE — SCL Service commun des laboratoires du ministère de l'Économie des Finances et de l'Industrie — Jeune Chambre Économique PLASTURGIE "Dans chaque innovation, la plasturgie est présente" — DECERNIS — CASIMIR LA VALEUR AJOUTÉE TECHNOLOGIQUE — SO BAG Le packaging autrement

INRA SCIENCE & IMPACT — SAFEFOODPACK DESIGN — .02 Sept 2015

LIST OF TASKS

Task 0 – Project management (INRA)

Task 1 – Deformulation of food packaging materials (LNE, SCL 33, ANIA, JCEP)

Task 2 – Application of FMECA approaches (LNE, INRA, AINIA, France Emballage, JCEP, Storsack)

Task 3 – Inference of expert rules (INRA, LNE)

Task 4 – Scaling D with solute geometry, T-Tg (INRA, UL)

Task 5 – Feeding large databases of K (UB, INRA)

Task 6 – Plasticization due to gas/aroma/lipid sorption (UL, UB, INRA)

Task 7 – Simulation engines (INRA)

Task 8 – Dissemination (CASIMIR, all)

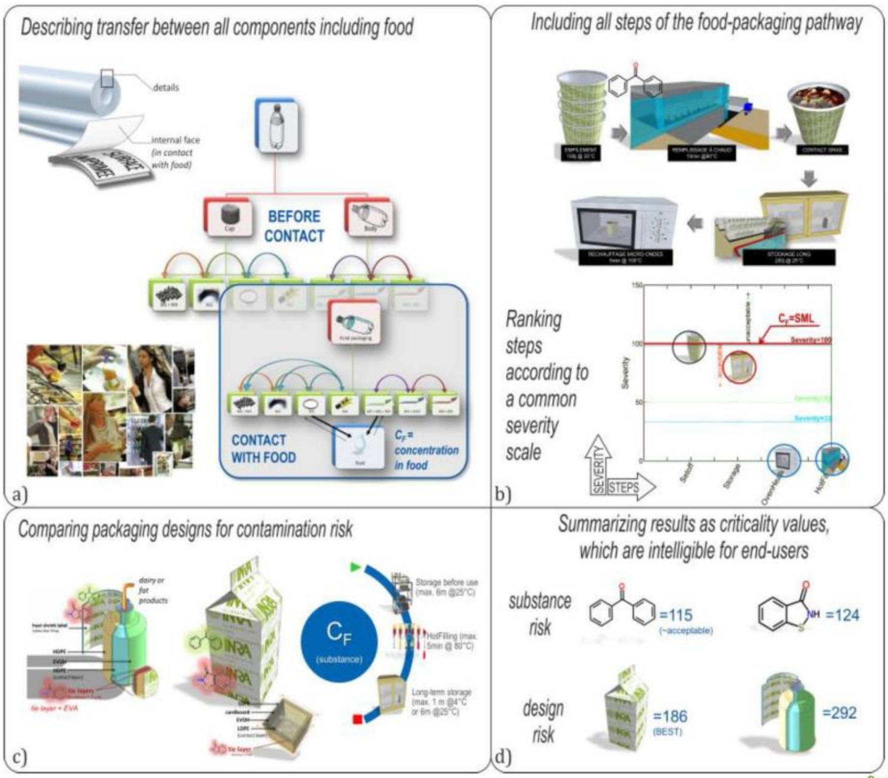
SAFEFOODPACK DESIGN

olivier.vitrac@agroparistech.fr
Sept 2015

INRA SCIENCE & IMPACT

.03 Sept 2015

GENERAL GOAL = PREVENTING MIGRATION



SAFEFOODPACK DESIGN

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Sept 2015

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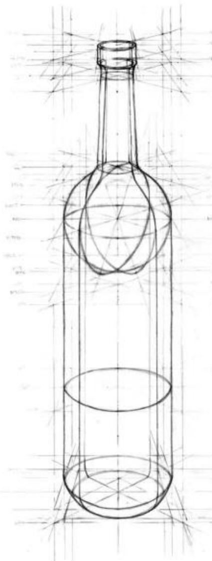
_00 ID OF THE PROJECT
_01 CONTEXT
_02 MIGRATION WITHOUT CONTACT
_03 BLIND DEFORMULATION
_04 MOLECULAR MODELING: D
_05 MOLECULAR MODELING: K
_06 PREVENTIVE APPROACHES
_07 GENERAL RECOMMENDATIONS



S A F E F O O D P A C K D E S I G N

_01

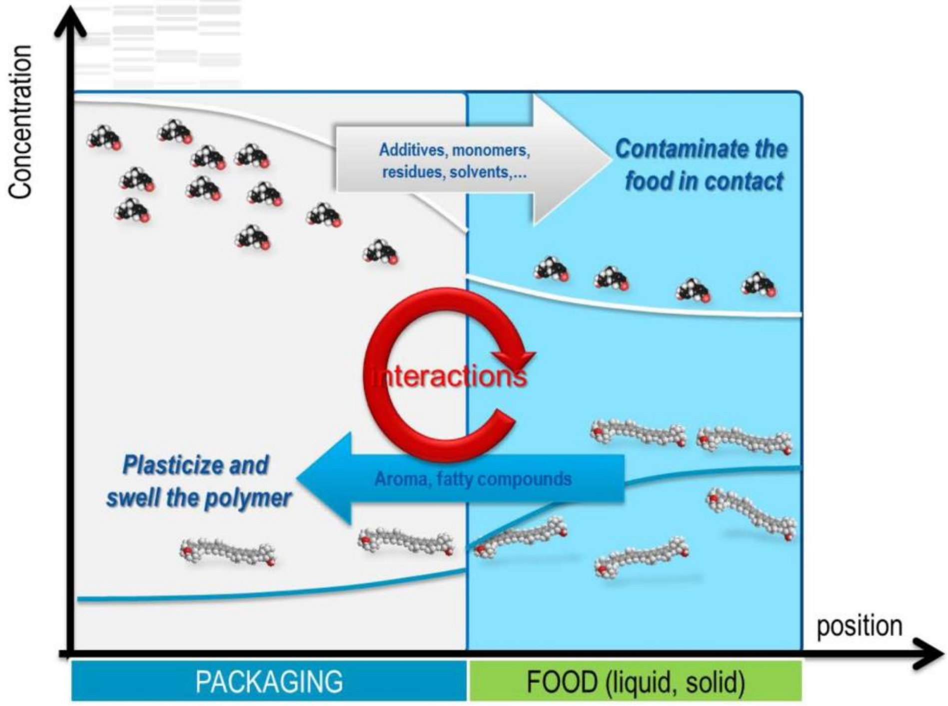
CONTEXT

WHY A NEW PROJECT?
WHY FOCUSING ON DESIGN?
HOW TO MANAGE THE COMPLEXITY OF THE SUPPLY CHAIN, MANY MATERIALS?

INRA SCIENCE & IMPACT

olivier.vitrac@agroparistech.fr / UMR 1145 Food Processing and Engineering

WHAT IS MIGRATION ?



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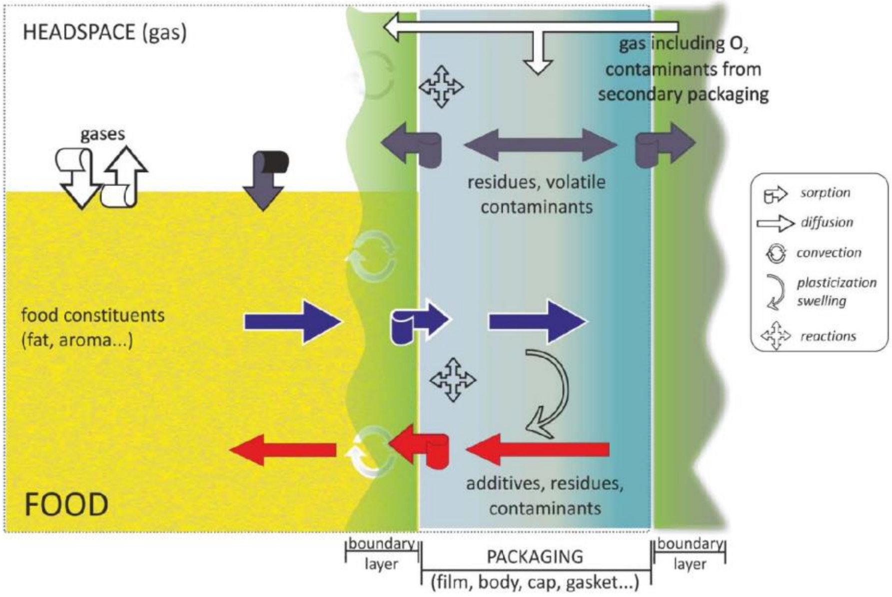
SAFEFOODPACK DESIGN

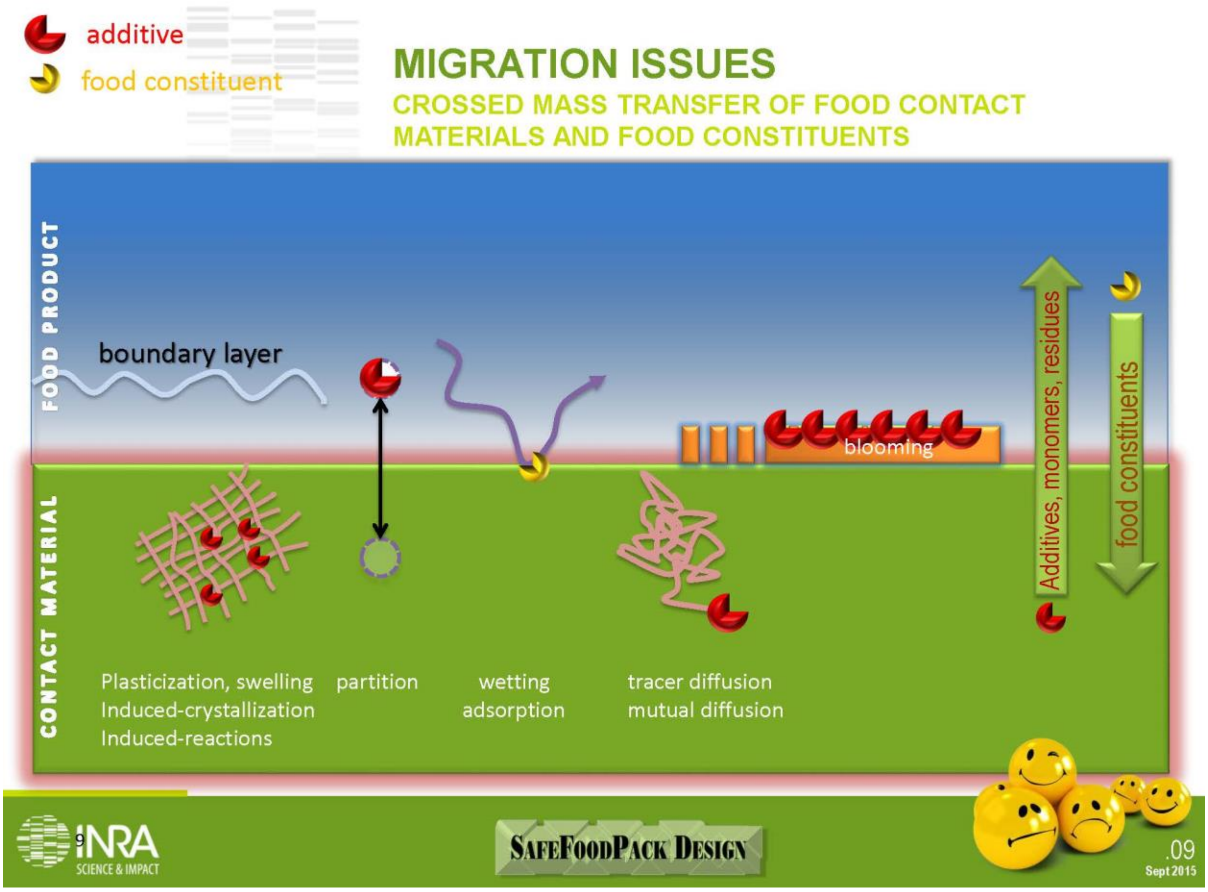
COUPLED MASS TRANSFER

between the food product and the packaging material



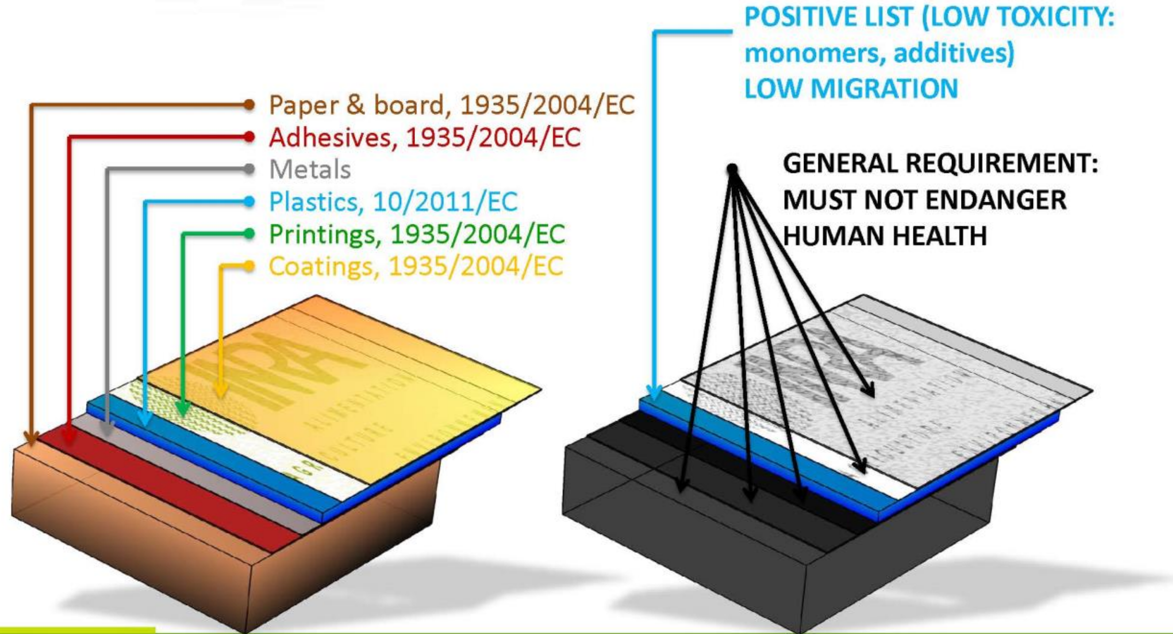
MIGRATION ISSUES

CROSSED MASS TRANSFER OF FOOD CONTACT MATERIALS AND FOOD CONSTITUENTS



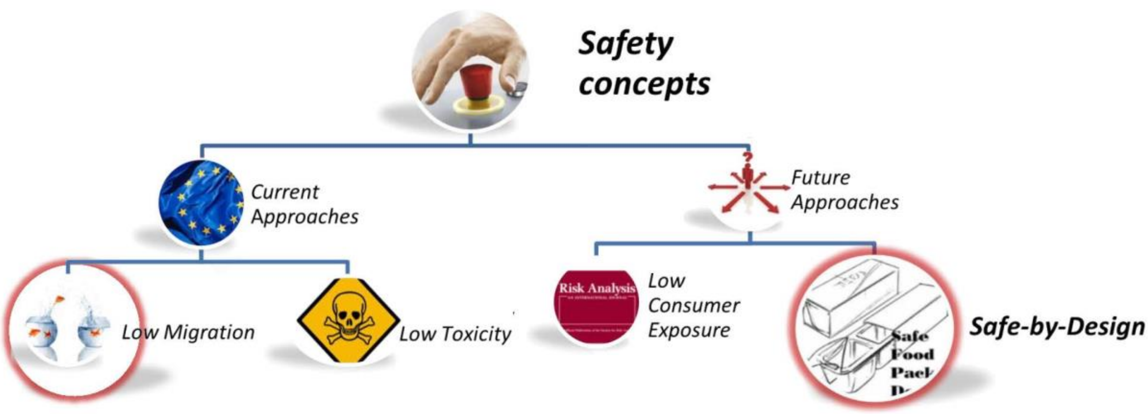
HETEROGENEOUS EU REGULATIONS

Variable concepts



TOWARDS NEW CONCEPTS

PREVENTIVE APPROACHES OF FOOD SAFETY



17 groups of materials listed in Annex 1 of regulation 1935/2004/EC are still not covered by specific measures. They must be produced according to **Good Manufacturing Practices** (Regulation 2023/2006/EC) incl. 3 pillars: quality assurance system, quality control system, documentation.


plastic
celluloses
adhesives
metals and alloys


UMR 1145 Food Processing and Engineering
CHAINED STEPS, COMBINED MATERIALS
Supply chain
Cap
Lid
Bottle body
INRA
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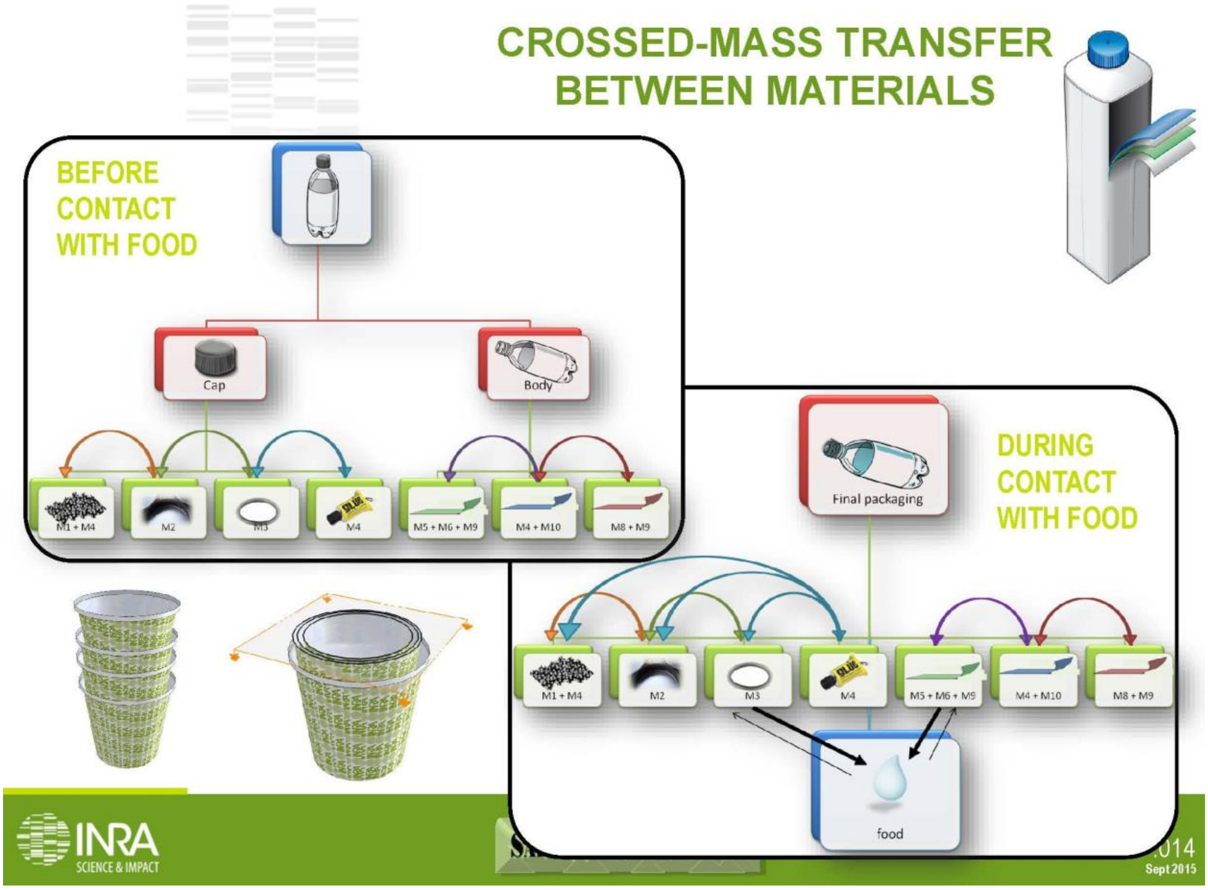
SafeFoodPack Design
.013
Sept 2015


CROSSED-MASS TRANSFER
BETWEEN MATERIALS
BEFORE
CONTACT
WITH FOOD
Cap
Body
M1 + M4
M2
M3
M4
M5 + M6 + M9
M4 + M10
M8 + M9
DURING
CONTACT
WITH FOOD
Final packaging
food
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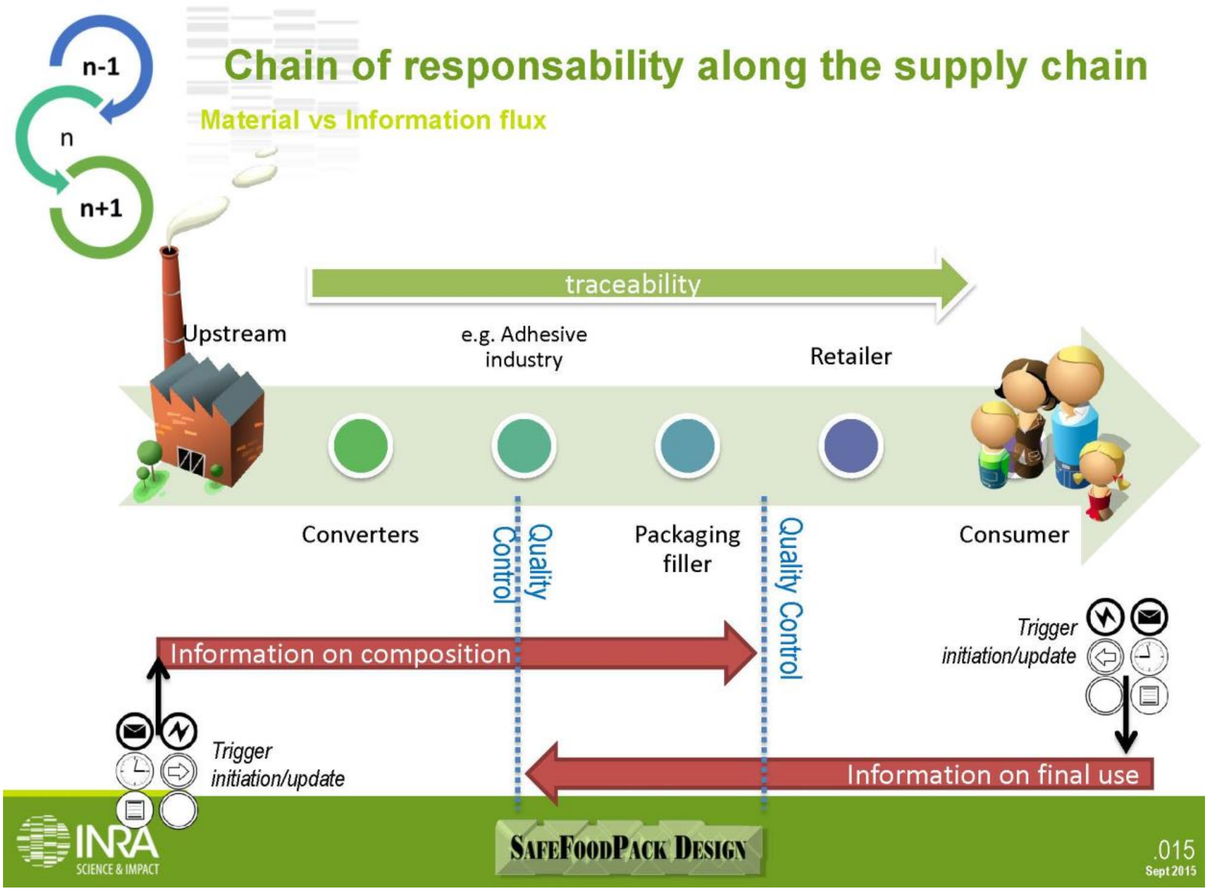
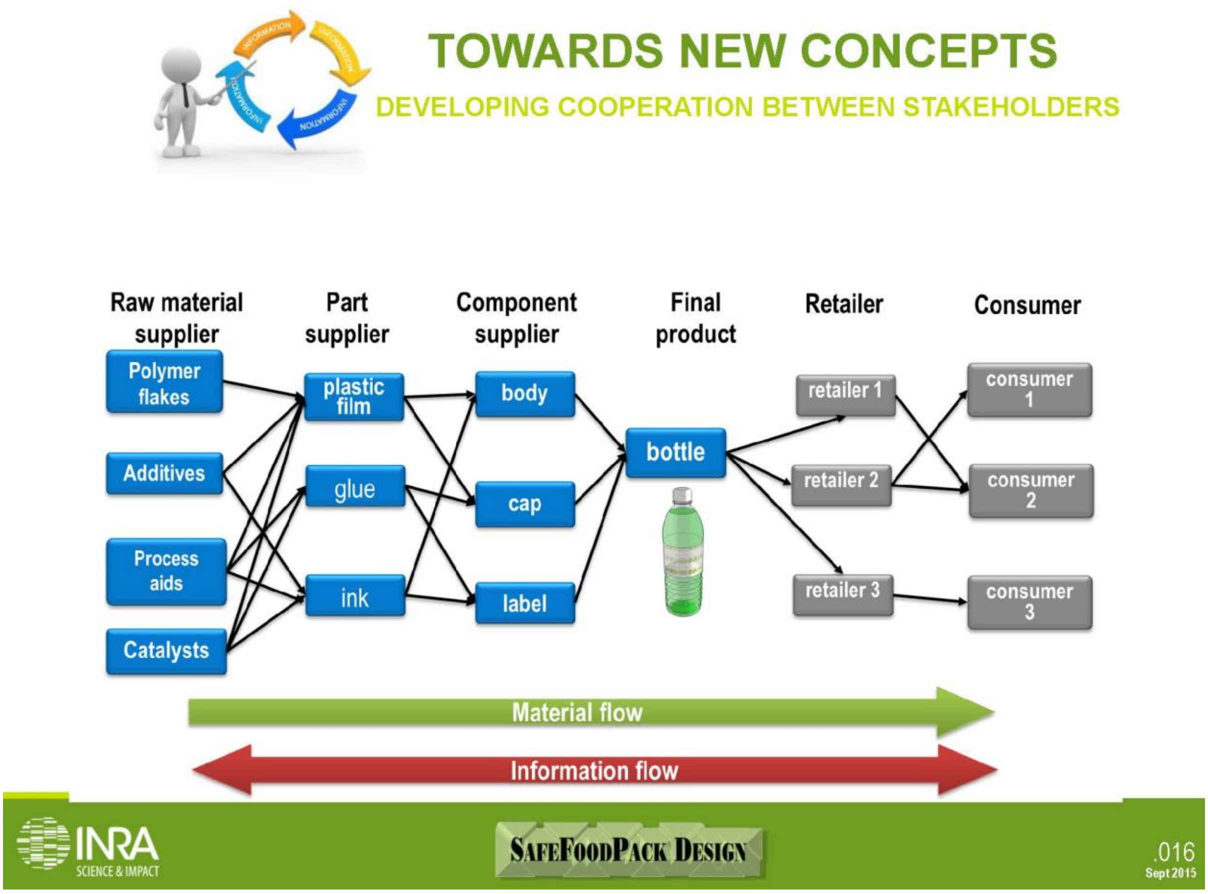
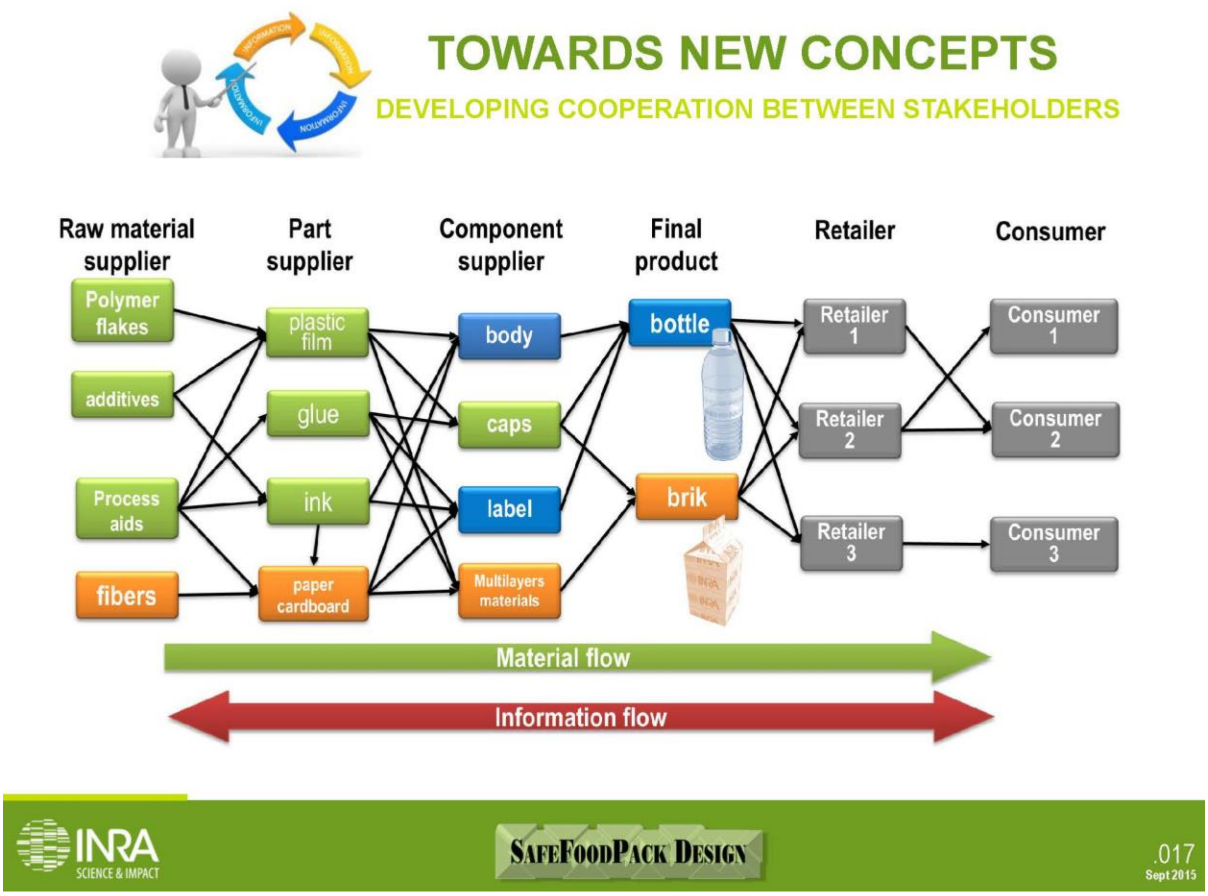
Sept 2015


Chain of responsability along the supply chain
Material vs Information flux
n-1
n
n+1
traceability
Upstream
e.g. Adhesive industry
Retailer
Converters
Quality Control
Packaging filler
Quality Control
Consumer
Trigger initiation/update
Information on composition
Trigger initiation/update
Information on final use
INRA
SCIENCE & IMPACT
SAFEFOODPACK DESIGN
.015
Sept 2015



TOWARDS NEW CONCEPTS
DEVELOPING COOPERATION BETWEEN STAKEHOLDERS
Raw material supplier
Part supplier
Component supplier
Final product
Retailer
Consumer
Polymer flakes
Additives
Process aids
Catalysts
plastic film
glue
ink
body
cap
label
bottle
retailer 1
retailer 2
retailer 3
consumer 1
consumer 2
consumer 3
Material flow
Information flow
INRA
SCIENCE & IMPACT
SafeFoodPack Design
.016
Sept 2015



TOWARDS NEW CONCEPTS
DEVELOPING COOPERATION BETWEEN STAKEHOLDERS
Raw material supplier
Part supplier
Component supplier
Final product
Retailer
Consumer
Polymer flakes
additives
Process aids
fibers
plastic film
glue
ink
paper cardboard
body
caps
label
Multilayers materials
bottle
brik
Retailer 1
Retailer 2
Retailer 3
Consumer 1
Consumer 2
Consumer 3
Material flow
Information flow
INRA
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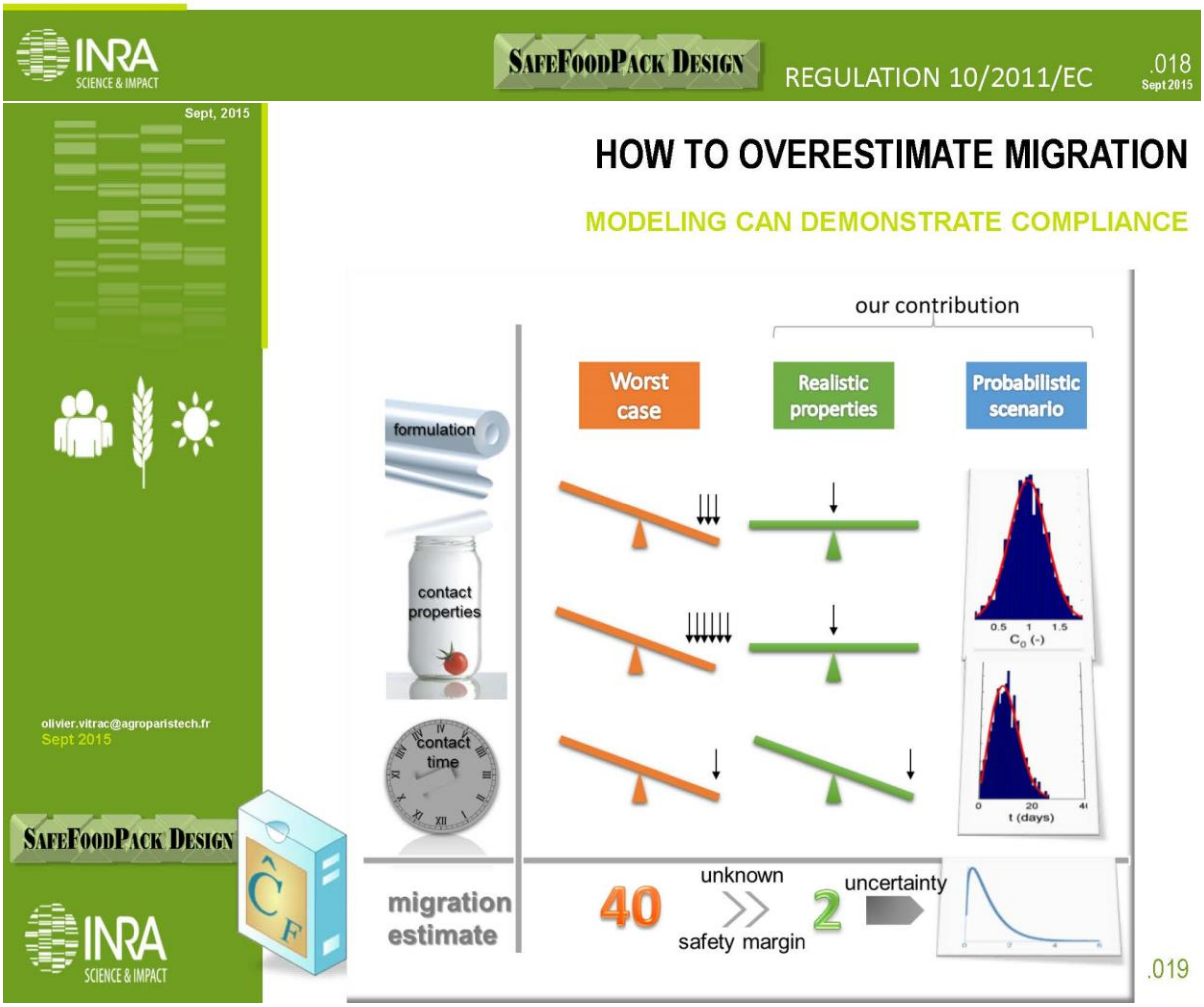
.017
Sept 2015

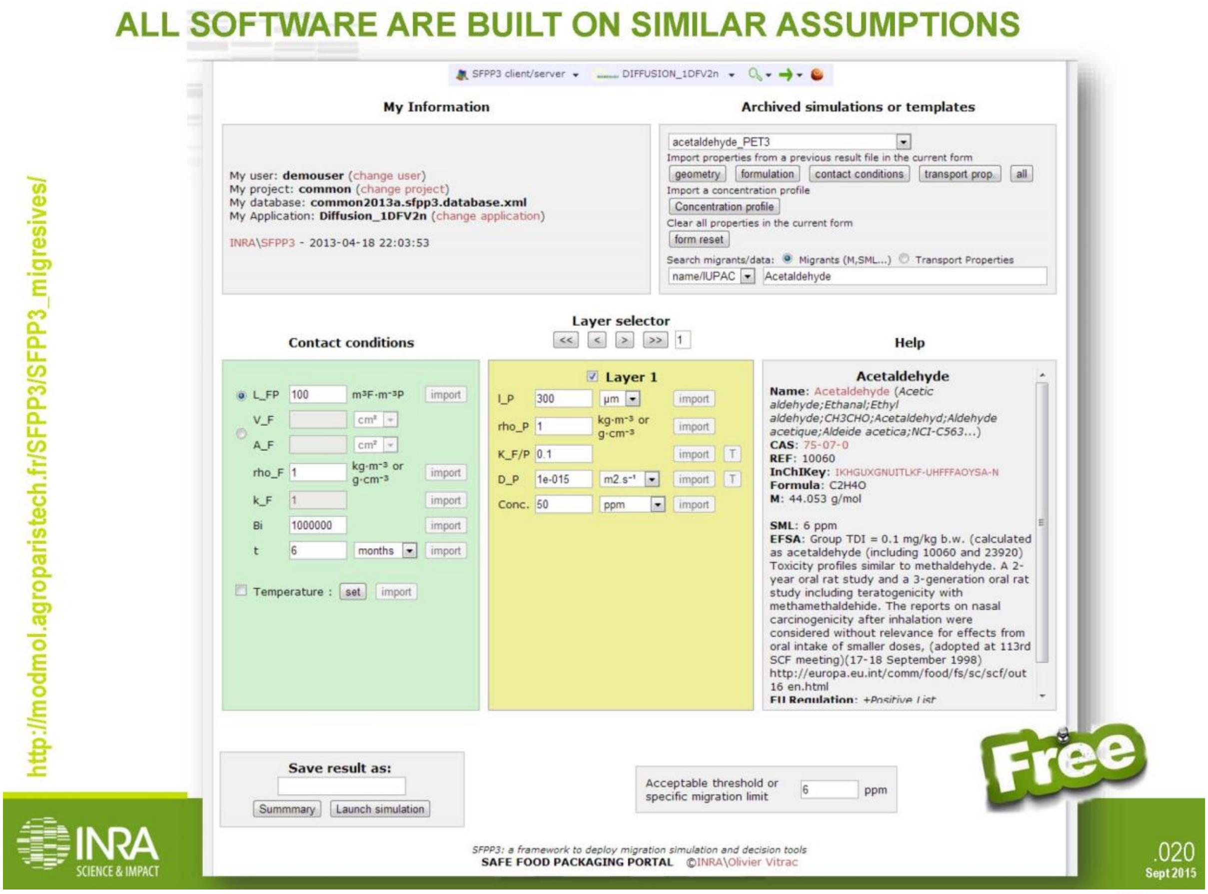
MIGRATION MODELING

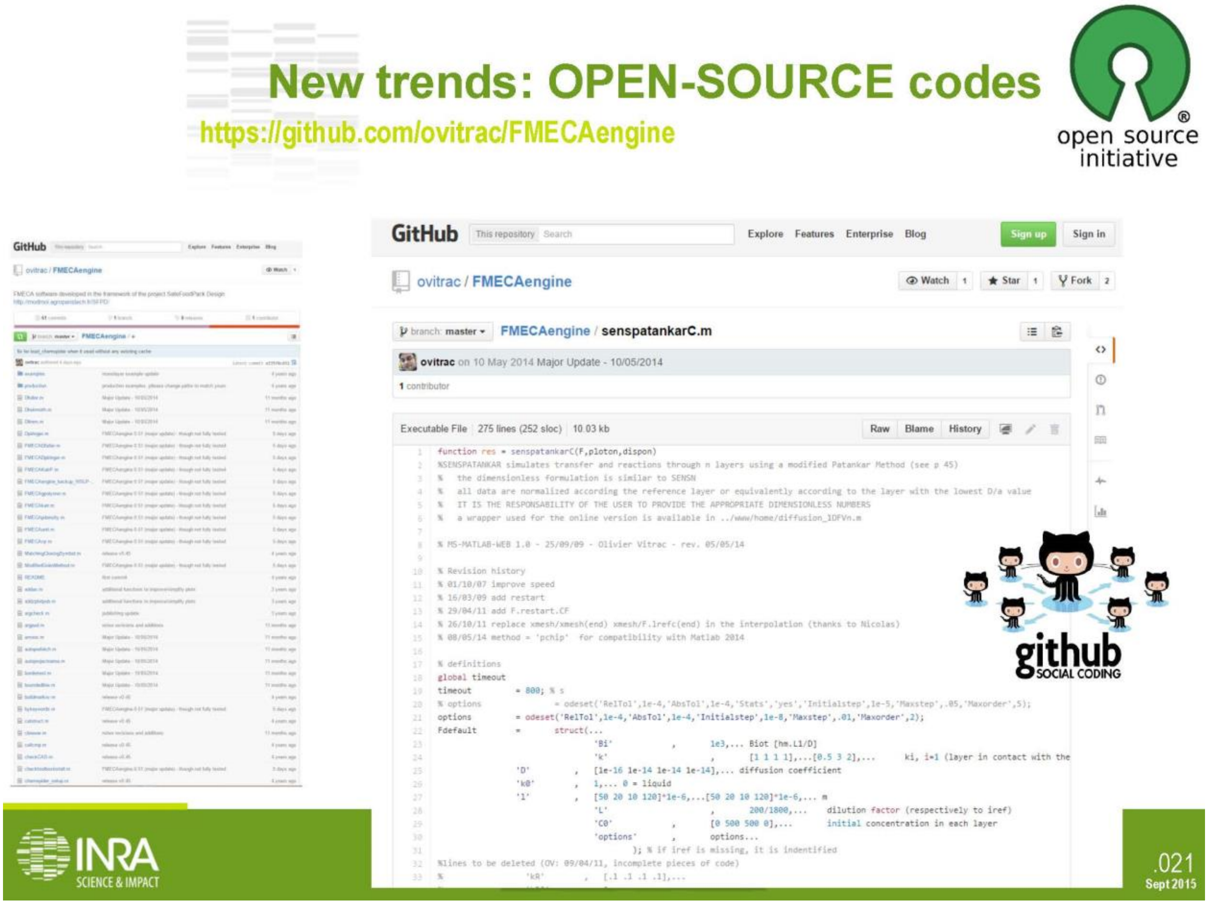
AUTHORIZED/RECOGNIZED IN EU, US, China

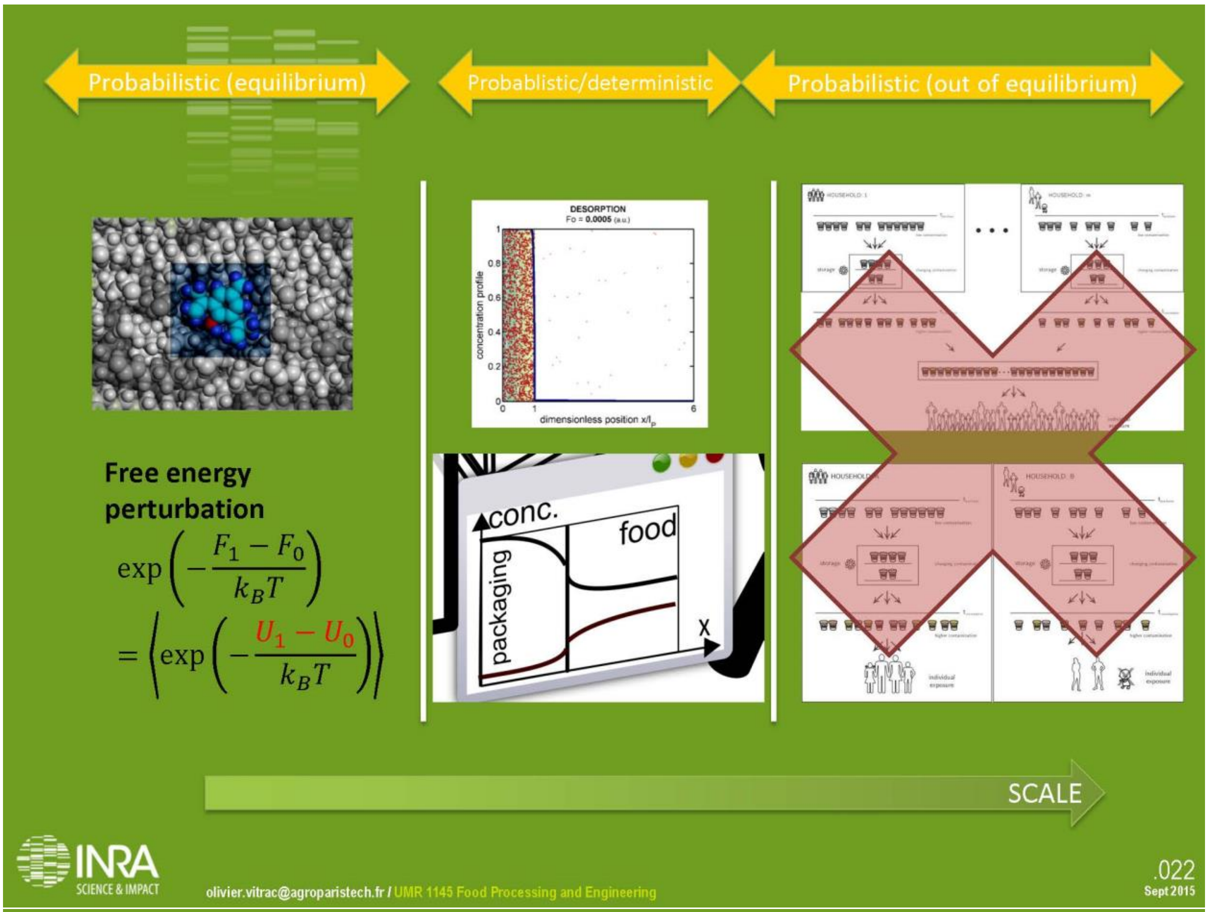
At each stage of manufacture, supporting documentation, substantiating the declaration of compliance, should be kept available for the enforcement authorities. Such demonstration of compliance July be based on migration testing. As migration testing is complex, costly and time consuming it should be admissible that compliance can be demonstrated also by calculations, including modelling, other analysis, and scientific evidence or reasoning if these render results which are at least as severe as the migration testing. Test results should be regarded as valid as long as formulations and processing conditions remain constant as part of a quality assurance system.

To screen for specific migration the migration potential can be calculated based on the residual content of the substance in the material or article applying generally recognised diffusion models based on scientific evidence that are constructed such as to overestimate real migration.

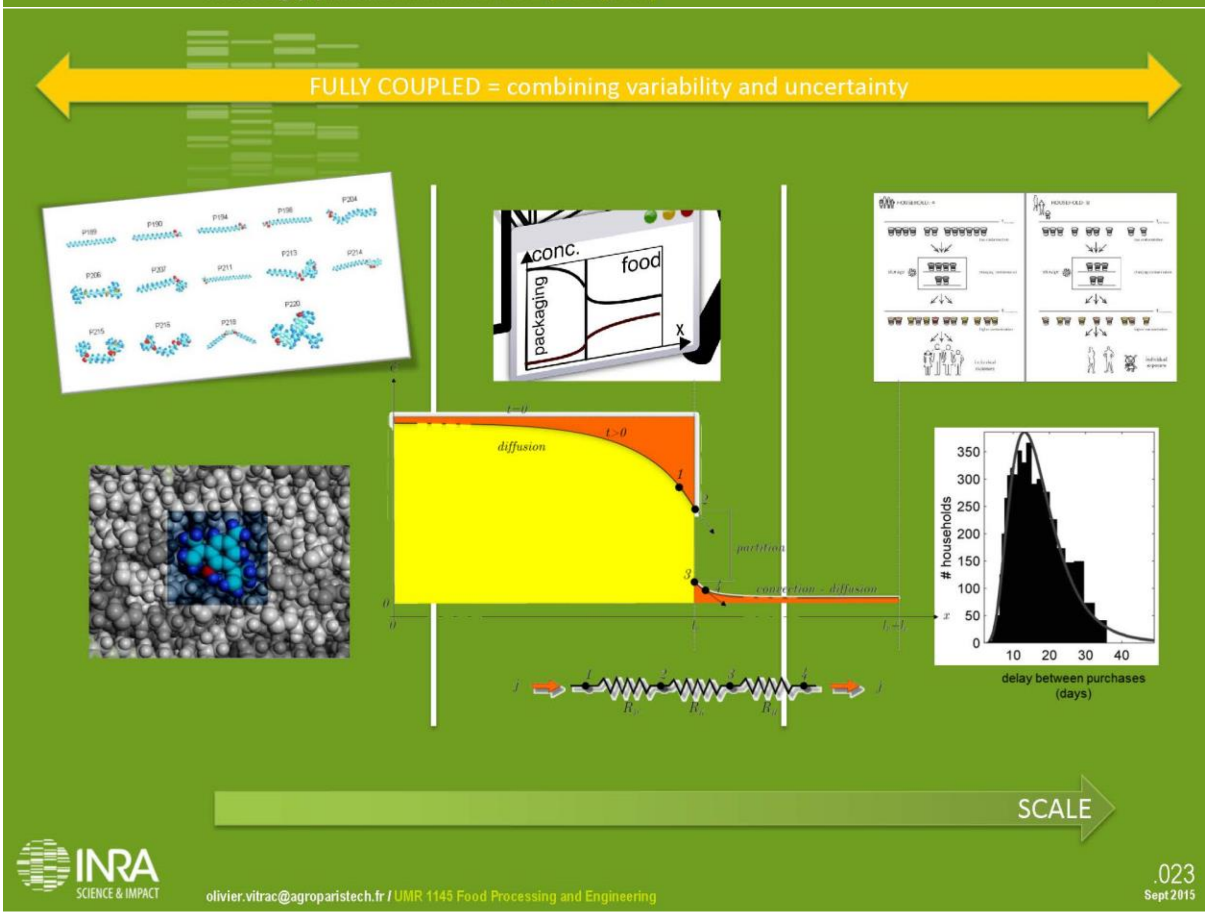



ALL SOFTWARE ARE BUILT ON SIMILAR ASSUMPTIONS
http://modmol.agroparistech.fr/SFPP3/SFPP3_migresives/
SFPP3 client/server
DIFFUSION_1DFV2n
My Information
My user: demouser (change user)
My project: common (change project)
My database: common2013a.sfpp3.database.xml
My Application: Diffusion_1DFV2n (change application)
INRA\SFPP3 - 2013-04-18 22:03:53
Archived simulations or templates
acetaldehyde_PET3
Import properties from a previous result file in the current form
geometry
formulation
contact conditions
transport prop.
all
Import a concentration profile
Concentration profile
Clear all properties in the current form
form reset
Search migrants/data: Migrants (M,SML...) Transport Properties
name/IUPAC
Acetaldehyde
Layer selector
Contact conditions
Help
Layer 1
Acetaldehyde
Name: Acetaldehyde (Acetic aldehyde;Ethanal;Ethyl aldehyde;CH3CHO;Acetaldehyd;Aldehyde acetique;Aldeide acetica;NCI-C563...)
CAS: 75-07-0
REF: 10060
InChIKey: IKHGUXGNUITLKF-UHFFFAOYSA-N
Formula: C2H4O
M: 44.053 g/mol
SML: 6 ppm
EFSA: Group TDI = 0.1 mg/kg b.w. (calculated as acetaldehyde (including 10060 and 23920) Toxicity profiles similar to methaldehyde. A 2-year oral rat study and a 3-generation oral rat study including teratogenicity with methamethaldehyde. The reports on nasal carcinogenicity after inhalation were considered without relevance for effects from oral intake of smaller doses, (adopted at 113rd SCF meeting)(17-18 September 1998) http://europa.eu.int/comm/food/fs/sc/scf/out16 en.html
Save result as:
Summary
Launch simulation
Acceptable threshold or specific migration limit
ppm
Free
SFPP3: a framework to deploy migration simulation and decision tools
SAFE FOOD PACKAGING PORTAL ©INRA\Olivier Vitrac
INRA SCIENCE & IMPACT
.020
Sept 2015


New trends: OPEN-SOURCE codes
https://github.com/ovitrac/FMECAengine
open source initiative
GitHub
ovitrac / FMECAengine
FMECAengine / senspatankarC.m
ovitrac on 10 May 2014 Major Update - 10/05/2014
1 contributor
Executable File 275 lines (252 sloc) 10.03 kb
github SOCIAL CODING
INRA SCIENCE & IMPACT
.021
Sept 2015



Probabilistic (equilibrium)
Probablistic/deterministic
Probabilistic (out of equilibrium)
DESORPTION
Fo = 0.0005 (a.u.)
concentration profile
dimensionless position x/l_p
Free energy perturbation
$\exp\left(-\frac{F_1-F_0}{k_BT}\right) = \left\langle \exp\left(-\frac{U_1-U_0}{k_BT}\right)\right\rangle$
conc.
food
packaging
x
SCALE
INRA
SCIENCE & IMPACT
olivier.vitrac@agroparistech.fr / UMR 1145 Food Processing and Engineering
.022
Sept 2015



FULLY COUPLED = combining variability and uncertainty
conc.
food
packaging
x
diffusion
partition
convection - diffusion
households
delay between purchases (days)
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_02

MIGRATION WITHOUT CONTACT

VOLATILE AND NON VOLATILE SUBSTANCES
HOW TO PREDICT AND CONTROL THEM ?

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MATBIM 2015, SAROGOSA, SPAIN

ANOTHER EXAMPLE

CONTAMINATION VIA PERMEATION

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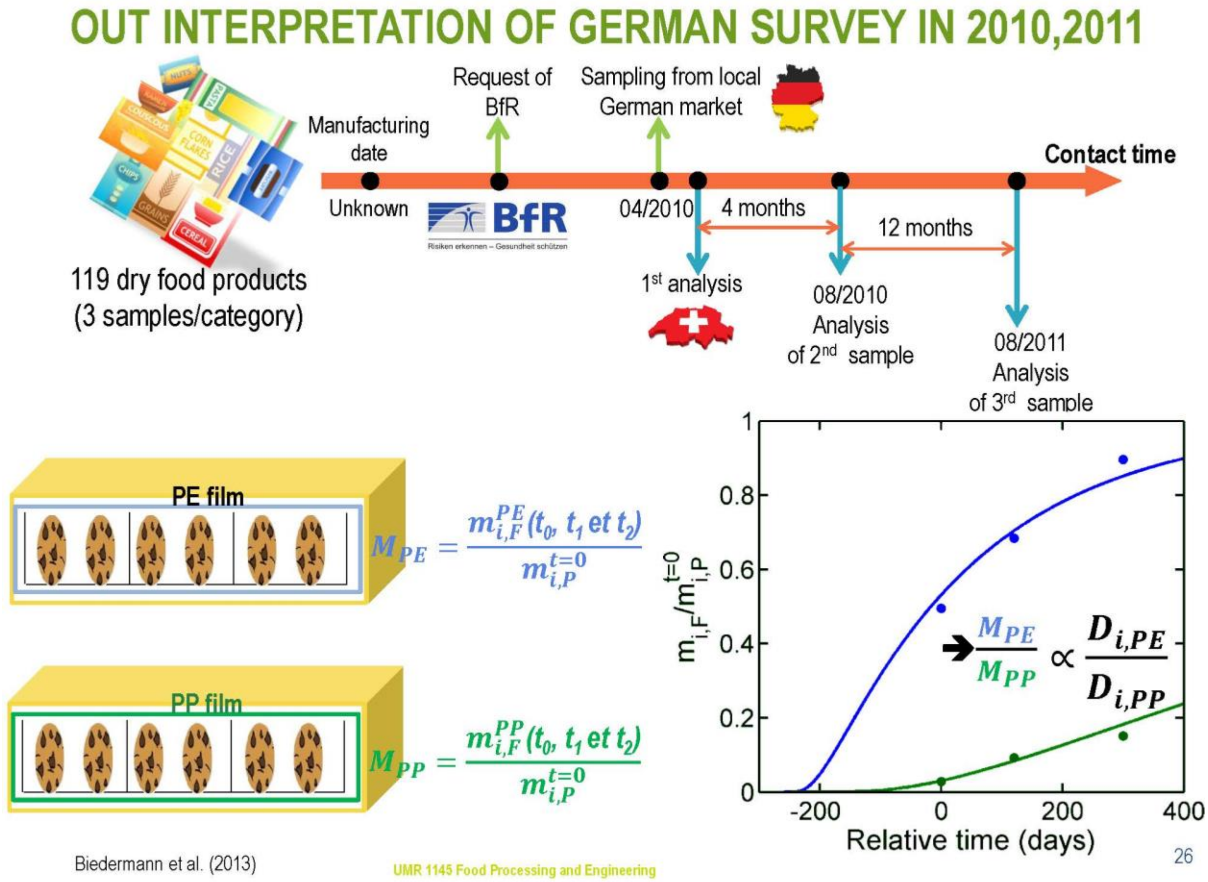
SAFEFOODPAC


OUT INTERPRETATION OF GERMAN SURVEY IN 2010,2011
119 dry food products
(3 samples/category)
Manufacturing date
Unknown
Request of BfR
BfR
Sampling from local German market
04/2010
4 months
12 months
Contact time
1st analysis
08/2010 Analysis of 2nd sample
08/2011 Analysis of 3rd sample
PE film
$M_{PE} = \frac{m_{i,F}^{PE}(t_0, t_1 \text{ et } t_2)}{m_{i,P}^{t=0}}$
PP film
$M_{PP} = \frac{m_{i,F}^{PP}(t_0, t_1 \text{ et } t_2)}{m_{i,P}^{t=0}}$
$m_{i,F}/m_{i,P}^{t=0}$
Relative time (days)
$\frac{M_{PE}}{M_{PP}} \propto \frac{D_{i,PE}}{D_{i,PP}}$
Biedermann et al. (2013)
UMR 1145 Food Processing and Engineering
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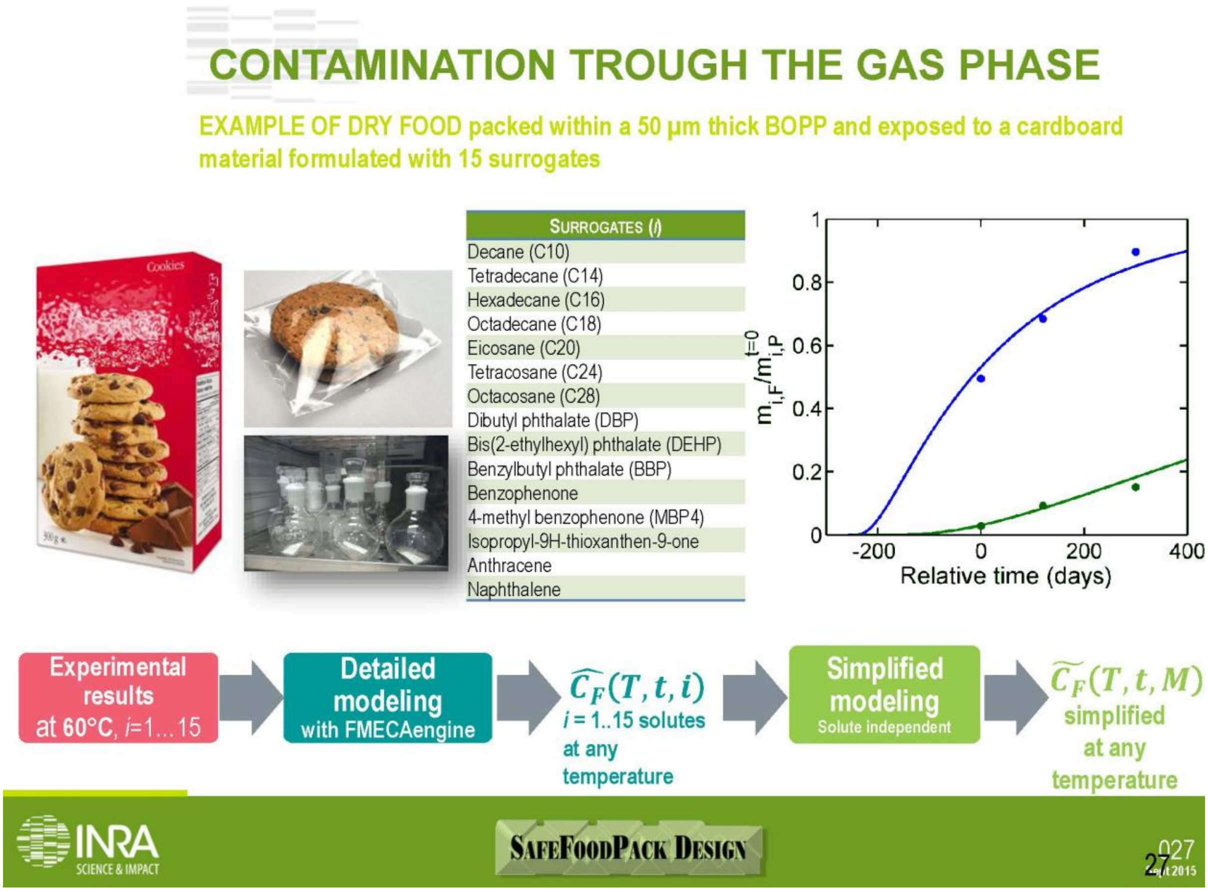
CONTAMINATION TROUGH THE GAS PHASE
EXAMPLE OF DRY FOOD packed within a 50 µm thick BOPP and exposed to a cardboard material formulated with 15 surrogates
Cookies
SURROGATES (i)
Decane (C10)
Tetradecane (C14)
Hexadecane (C16)
Octadecane (C18)
Eicosane (C20)
Tetracosane (C24)
Octacosane (C28)
Dibutyl phthalate (DBP)
Bis(2-ethylhexyl) phthalate (DEHP)
Benzylbutyl phthalate (BBP)
Benzophenone
4-methyl benzophenone (MBP4)
Isopropyl-9H-thioxanthen-9-one
Anthracene
Naphthalene
$m_{i,F}/m_{i,P}^{t=0}$
Relative time (days)
Experimental results at 60°C, i=1…15
Detailed modeling with FMECAengine
$\widehat{C_F}(T,t,i)$
i = 1..15 solutes at any temperature
Simplified modeling Solute independent
$\widetilde{C_F}(T,t,M)$
simplified at any temperature
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SAFEFOODPACK DESIGN
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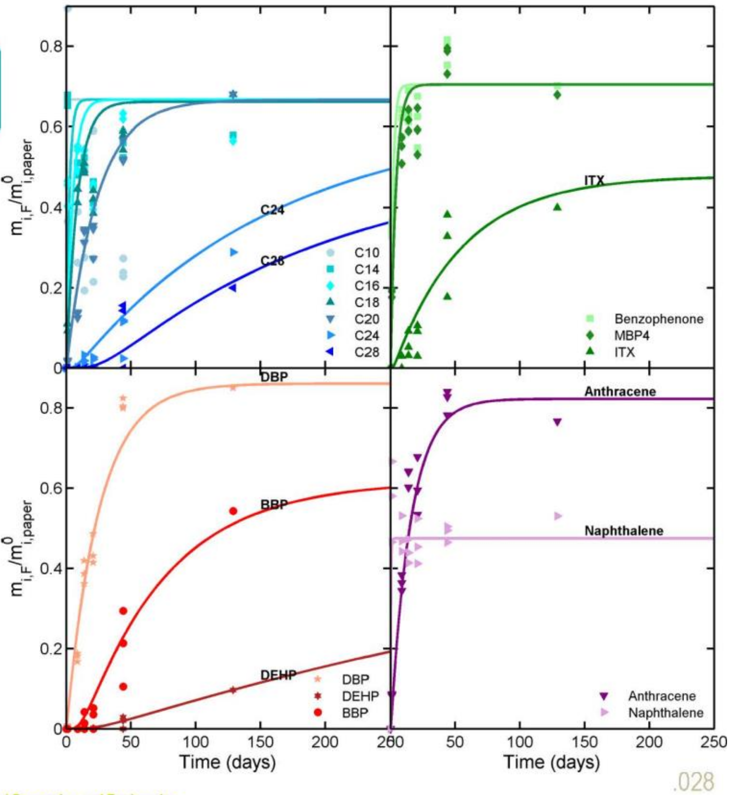
PREDICTIONS vs EXPERIMENTS

Nguyen *et al.* 2014, submitted to I&EC, FAC

Experimental results at 60°C, i=1…15 → Detailed modeling with FMECAengine

$$\frac{m_{i,F}^{(t)}}{m_{i,P}^{0}} = \frac{V_F}{m_{i,P}^{0}} \int_0^t C_{i,F}^{(t)} d\tau$$

0 to 120 days



INRA

https://github.com/ovitrac/FMECAengine

Food Processing and Engineering

.028

TWO EXTREME CASES

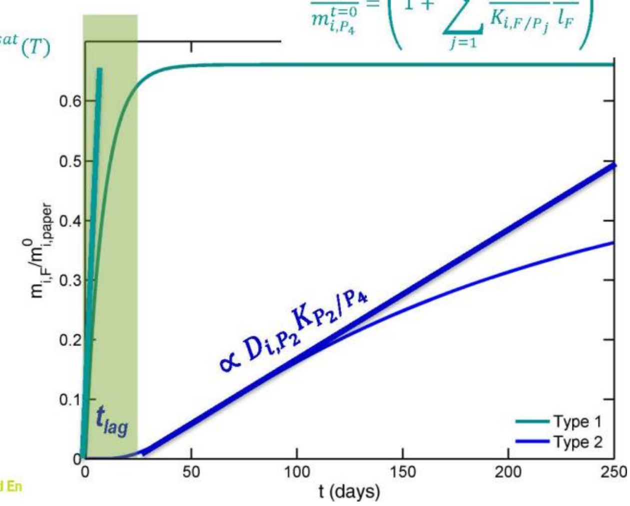
Type 1 : desorption in gaseous phase (exponential without delay)

$$\frac{C_{i,P_4}^{t=0} - C_{i,P_4}(t)}{C_{i,P_4}^{t=0} - C_{i,P_4}^{eq}} \xrightarrow[t\to 0]{} \frac{P_i^{vsat}(T) V_i \gamma_{i,P_4}^{v}(T) h_e}{(1-\varepsilon_{P_4}) RT l_{P_4}} \left(1 + K_{P_4/F} L_{P_4/F}\right) t$$

$$\frac{m_{i,F}^{eq}}{m_{i,P_4}^{t=0}} = \left(1 + \sum_{j=1}^{4} \frac{1}{K_{i,F/P_j}} \frac{l_{P_j}}{l_F}\right)^{-1}$$

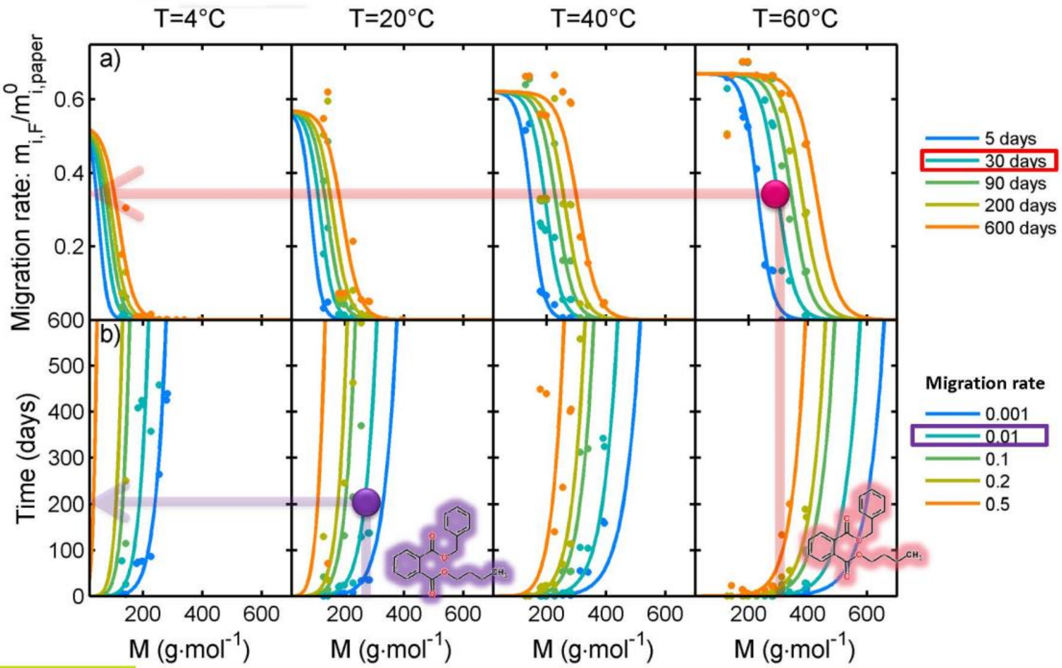
$$\frac{dm_{i,F}(t)}{dt}\Big|_{t\to 0} \propto P_i^{vsat}(T)$$

Type 2 : diffusion through the PP layer



UMR 1145 Food Processing and En

ISO-MIGRATION: TIME x TEMPERATURE x M
ISO-TIME: CONTAMINATION x TEMPERATURE x M



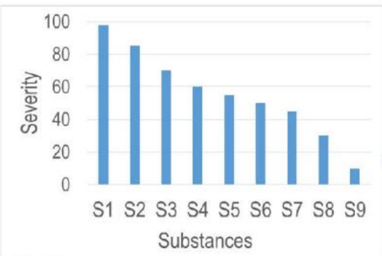
22 INRA SCIENCE & IMPACT SafeFoodPack Design

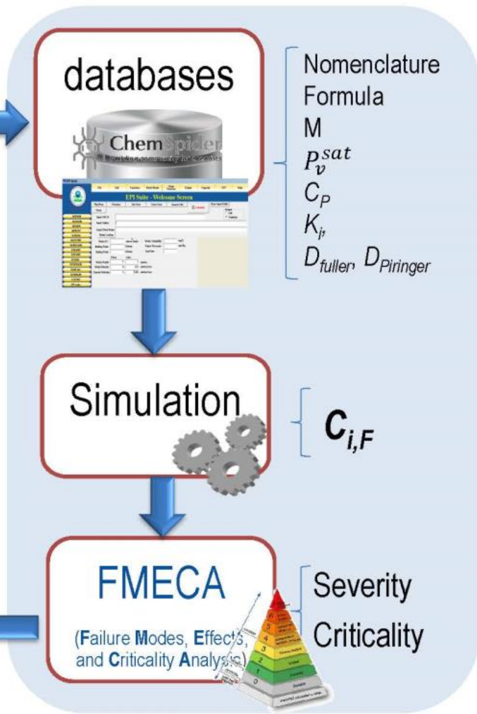
Example: benzyle butyle phtalate (M = 313 g·mol^{-1})

.030 Sept 2015

FMECAengine can manage volatiles

Substances	Description	Quanti
S1	UV-stabilizer	10
S2	UV-stabilize	20
S3	Antibiocide	5
S4	Antibiocide	1
S5	Mineral oil	4
S6	Mineral oil	6
S7	Solvent	5
S8	Solvent	5
S9	Photoinitiator	10





Nguyen P-M et *al.*, AIChE J. 2013, 59 (4), 1183

"FMECAengine" open-source project https://github.com/ovitrac/FMECAengine .031

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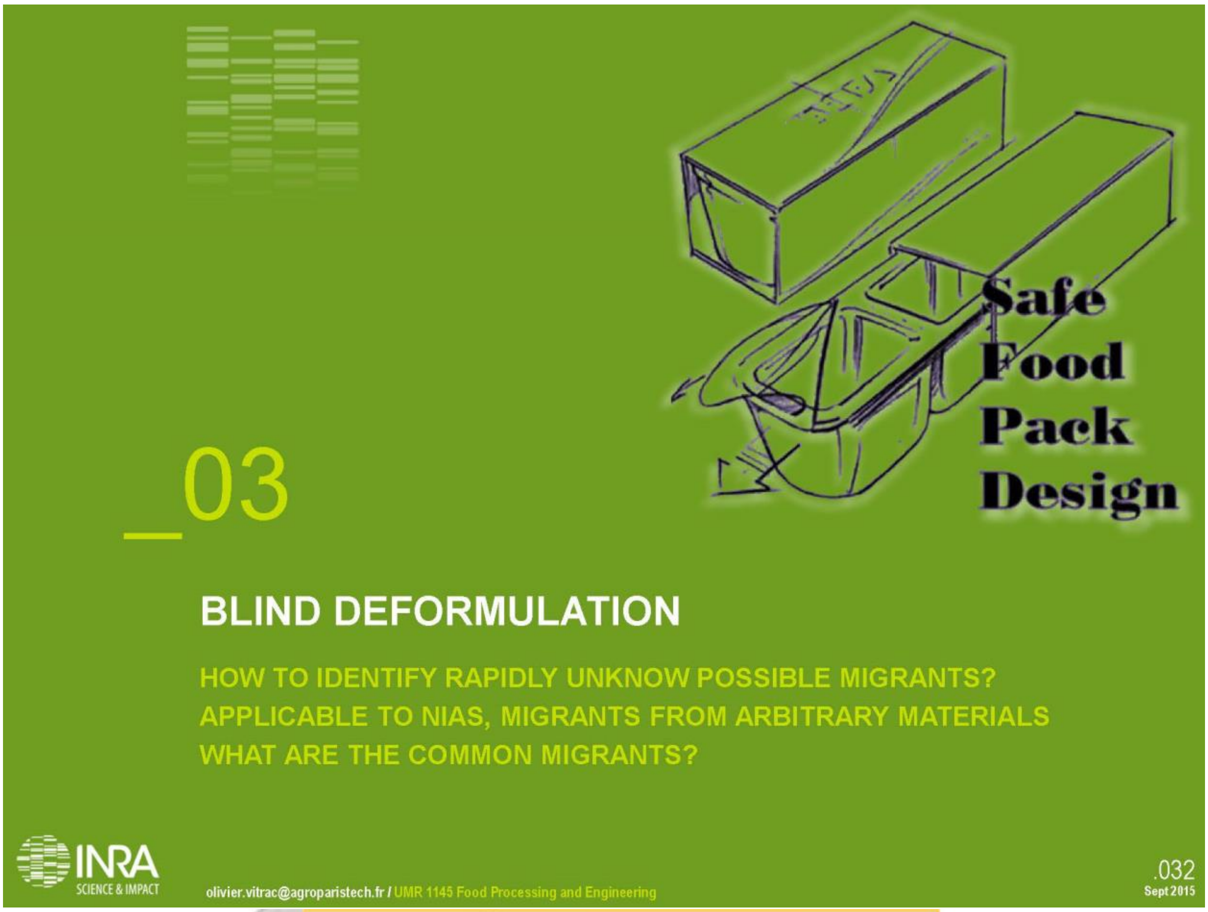
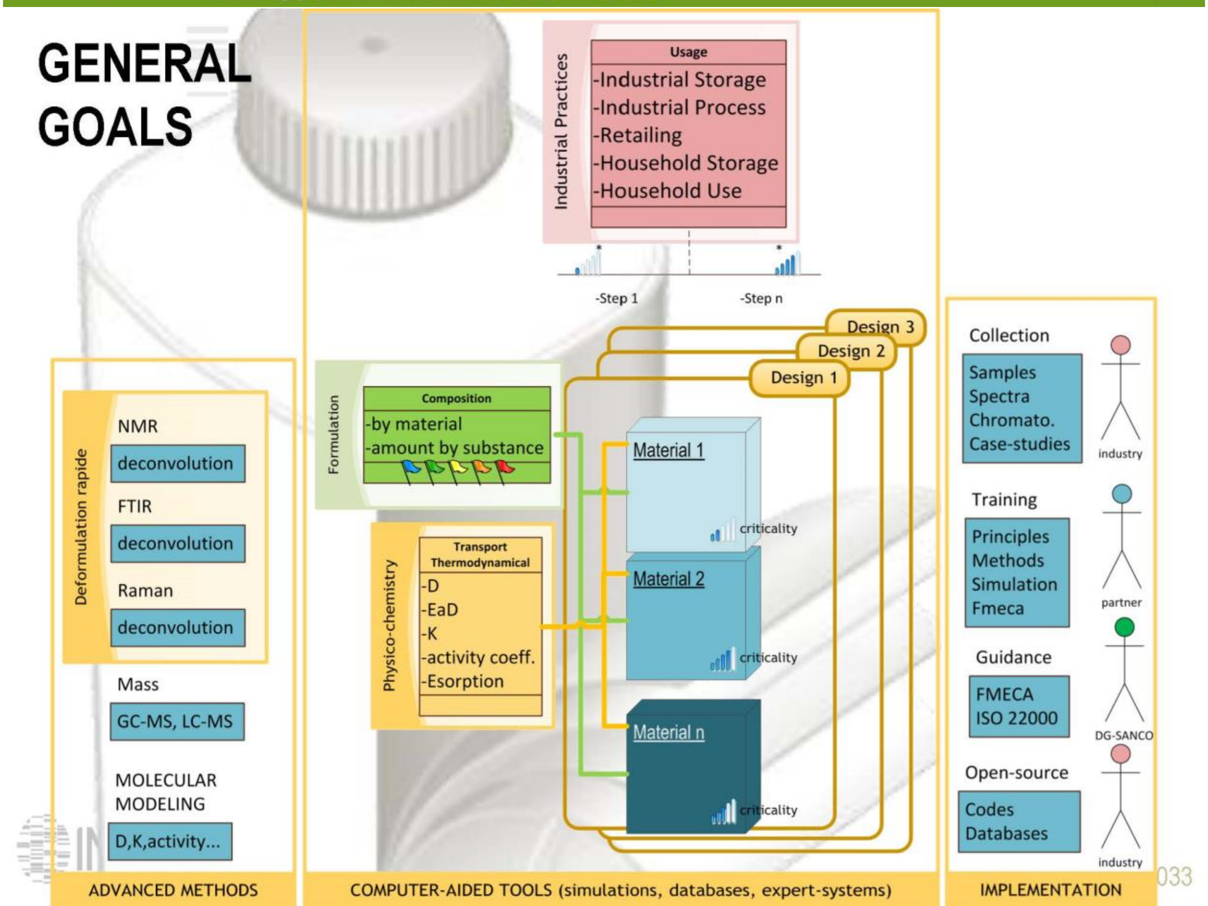
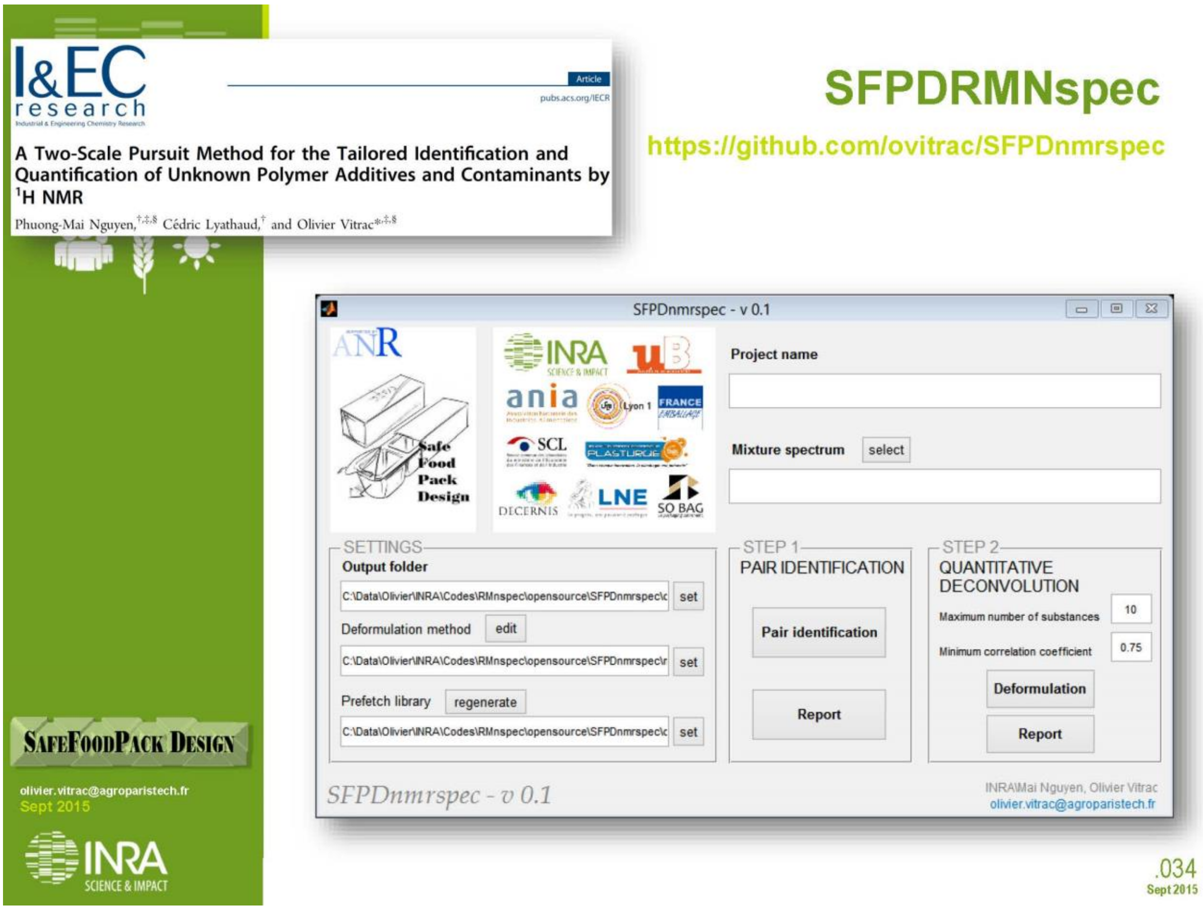
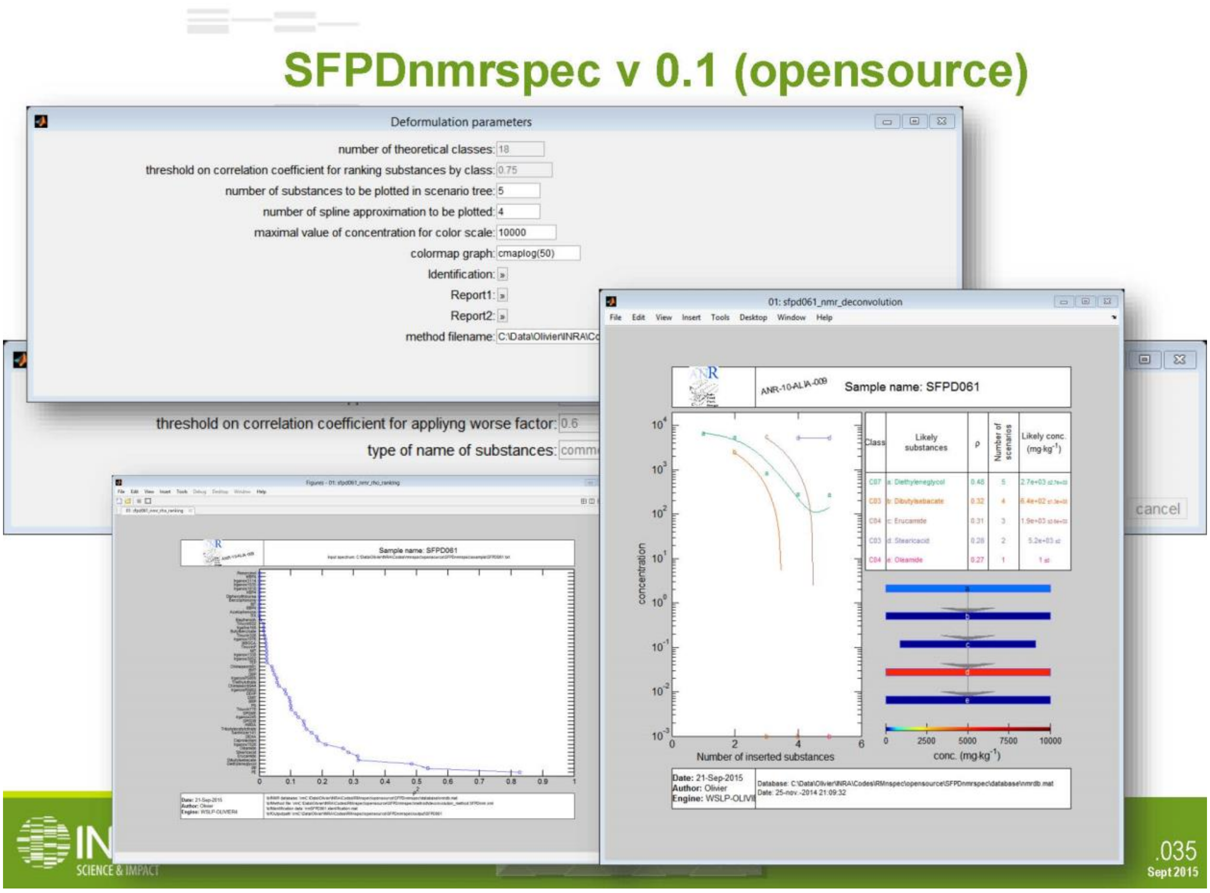
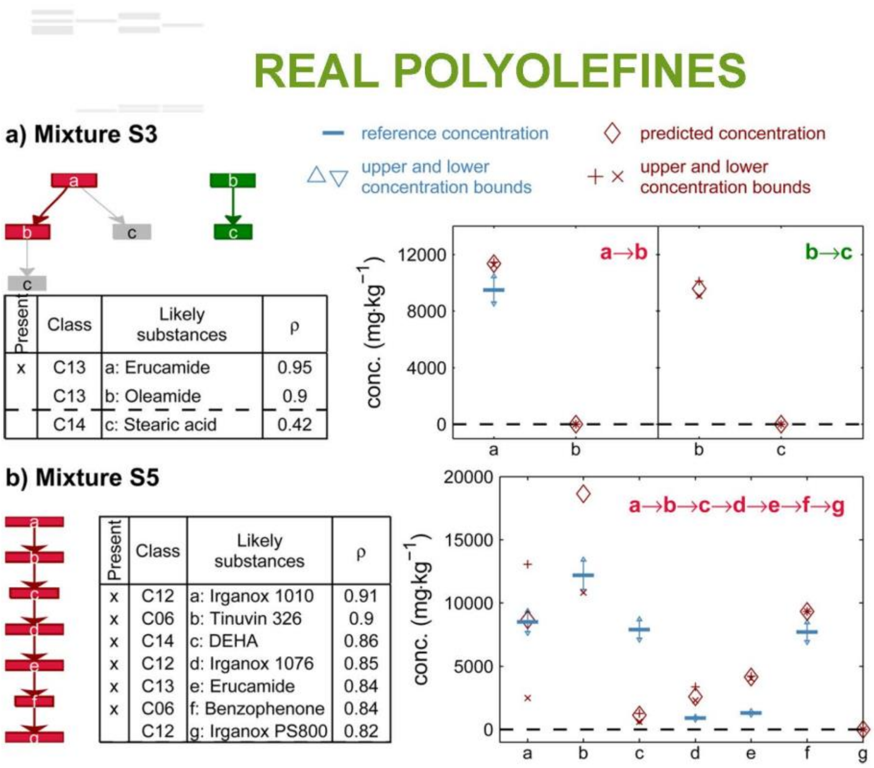
UMR 1145 Food Processing and Engineering


Safe Food Pack Design
_03
BLIND DEFORMULATION
HOW TO IDENTIFY RAPIDLY UNKNOW POSSIBLE MIGRANTS?
APPLICABLE TO NIAS, MIGRANTS FROM ARBITRARY MATERIALS
WHAT ARE THE COMMON MIGRANTS?
INRA SCIENCE & IMPACT
olivier.vitrac@agroparistech.fr / UMR 1145 Food Processing and Engineering
.032
Sept 2015


GENERAL GOALS
Industrial Practices
Usage
-Industrial Storage
-Industrial Process
-Retailing
-Household Storage
-Household Use
-Step 1
-Step n
Design 3
Design 2
Design 1
Formulation
Composition
-by material
-amount by substance
Physico-chemistry
Transport Thermodynamical
-D
-EaD
-K
-activity coeff.
-Esorption
Material 1
criticality
Material 2
criticality
Material n
criticality
Deformulation rapide
NMR
deconvolution
FTIR
deconvolution
Raman
deconvolution
Mass
GC-MS, LC-MS
MOLECULAR MODELING
D,K,activity...
Collection
Samples
Spectra
Chromato.
Case-studies
industry
Training
Principles
Methods
Simulation
Fmeca
partner
Guidance
FMECA
ISO 22000
DG-SANCO
Open-source
Codes
Databases
industry
ADVANCED METHODS
COMPUTER-AIDED TOOLS (simulations, databases, expert-systems)
IMPLEMENTATION
033

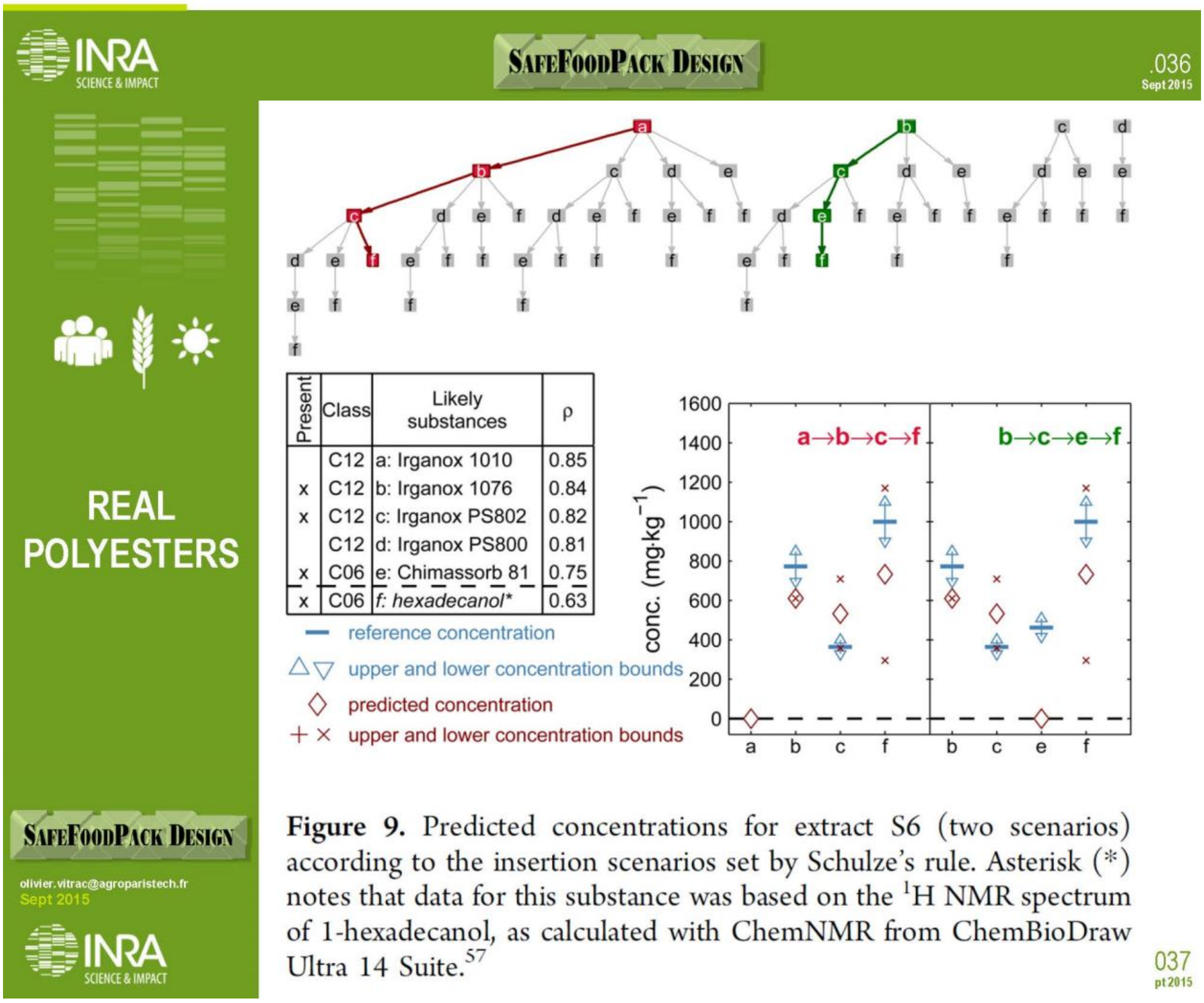

I&EC research
Article
pubs.acs.org/IECR
A Two-Scale Pursuit Method for the Tailored Identification and Quantification of Unknown Polymer Additives and Contaminants by ¹H NMR
Phuong-Mai Nguyen, Cédric Lyathaud, and Olivier Vitrac
SFPDRMNspec
https://github.com/ovitrac/SFPDnmrspec
SFPDnmrspec - v 0.1
Project name
Mixture spectrum
select
SETTINGS
Output folder
set
Deformulation method
edit
Prefetch library
regenerate
STEP 1
PAIR IDENTIFICATION
Pair identification
Report
STEP 2
QUANTITATIVE DECONVOLUTION
Maximum number of substances
10
Minimum correlation coefficient
0.75
Deformulation
Report
SFPDnmrspec - v 0.1
INRA\Mai Nguyen, Olivier Vitrac
olivier.vitrac@agroparistech.fr
SAFEFOODPACK DESIGN
olivier.vitrac@agroparistech.fr
Sept 2015
INRA SCIENCE & IMPACT
.034
Sept 2015


SFPDnmrspec v 0.1 (opensource)
Deformulation parameters
number of theoretical classes: 18
threshold on correlation coefficient for ranking substances by class: 0.75
number of substances to be plotted in scenario tree: 5
number of spline approximation to be plotted: 4
maximal value of concentration for color scale: 10000
colormap graph: cmaplog(50)
Identification:
Report1:
Report2:
method filename:
threshold on correlation coefficient for appliyng worse factor: 0.6
type of name of substances:
cancel
01: sfpd061_nmr_deconvolution
Sample name: SFPD061
Number of inserted substances
concentration
conc. (mg·kg⁻¹)
Likely substances
Likely conc. (mg·kg⁻¹)
.035
Sept 2015



Present	Class	Likely substances	ρ
x	C13	a: Erucamide	0.95
	C13	b: Oleamide	0.9
	C14	c: Stearic acid	0.42

Present	Class	Likely substances	ρ
x	C12	a: Irganox 1010	0.91
x	C06	b: Tinuvin 326	0.9
x	C14	c: DEHA	0.86
x	C12	d: Irganox 1076	0.85
x	C13	e: Erucamide	0.84
x	C06	f: Benzophenone	0.84
	C12	g: Irganox PS800	0.82



Present	Class	Likely substances	ρ
	C12	a: Irganox 1010	0.85
x	C12	b: Irganox 1076	0.84
x	C12	c: Irganox PS802	0.82
	C12	d: Irganox PS800	0.81
x	C06	e: Chimassorb 81	0.75
x	C06	*f: hexadecanol**	0.63

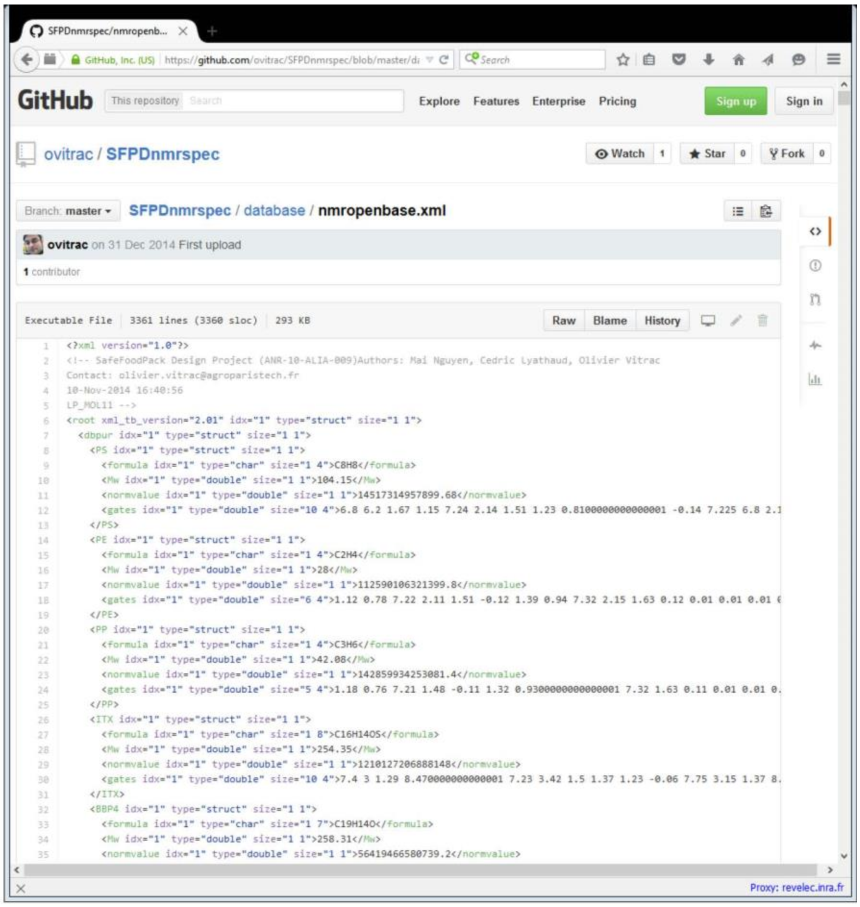
Figure 9. Predicted concentrations for extract S6 (two scenarios) according to the insertion scenarios set by Schulze's rule. Asterisk (*) notes that data for this substance was based on the ^{1}H NMR spectrum of 1-hexadecanol, as calculated with ChemNMR from ChemBioDraw Ultra 14 Suite.[57]

Sept, 2015

olivier.vitrac@agroparistech.fr
Sept 2015

SAFEFOODPACK DESIGN

INRA SCIENCE & IMPACT

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<?xml version="1.0"?>
<!-- SafeFoodPack Design Project (ANR-10-ALIA-009)Authors: Mai Nguyen, Cedric Lyathaud, Olivier Vitrac
Contact: olivier.vitrac@agroparistech.fr
10-Nov-2014 16:40:56
LP_MOL11 -->
<root xml_tb_version="2.01" idx="1" type="struct" size="1 1">
  <dbpur idx="1" type="struct" size="1 1">
    <PS idx="1" type="struct" size="1 1">
      <formula idx="1" type="char" size="1 4">C8H8</formula>
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    </PS>
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    </ITX>
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      <normvalue idx="1" type="double" size="1 1">56419466580739.2</normvalue>
```


SAFEFOODPACK DESIGN

olivier.vitrac@agroparistech.fr
Sept 2015

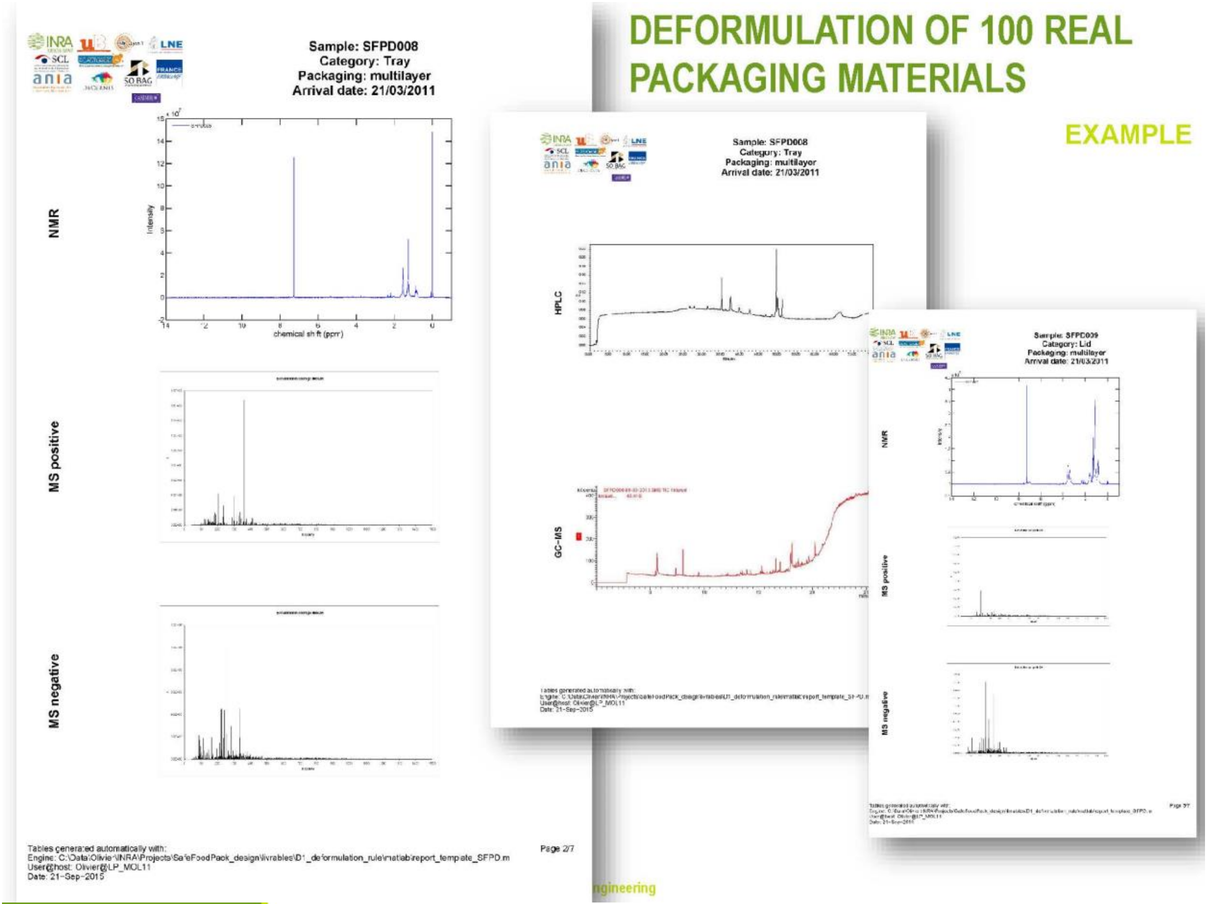
INRA SCIENCE & IMPACT

DEFORMULATION OF 100 REAL PACKAGING MATERIALS

SUMMARY

- **>110 samples collected**, 97 samples extracted
- **Fast blind deformulation** (NMR, FTIR, Raman, direct infusion in MS) via generalized correlations (weighted, regularized, sparse solutions)
- **PIPELINES to NMR and MS libraries**
- **Libraries of fingerprints**: calibrated spectra (+400 NMR, +90 FTIR) and chromatograms (GC-MS: 250 substances, HPLC-UV: retention times of ~100 substances)
- **All data have been integrated within an EXPERT SYSTEM**, which can be interrogated using “natural language”
- **Automatic PIPELINES to simulation engines**

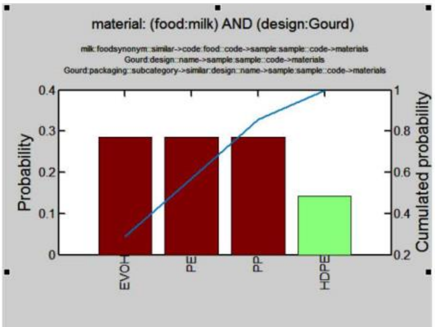
.039
Sept 2015


DEFORMULATION OF 100 REAL PACKAGING MATERIALS
EXAMPLE
Sample: SFPD008
Category: Tray
Packaging: multilayer
Arrival date: 21/03/2011
NMR
MS positive
MS negative
HPLC
GC-MS
Sample: SFPD009
Category: Lid
Packaging: multilayer
Arrival date: 21/03/2011
Tables generated automatically with:
Date: 21-Sep-2015
Page 2/7


EXPERT SYSTEM
OVERVIEW
FOOD
milk
ham
babyfood
Biscuit
mustard
DESIGN
bag with gusset
compartimentalized tray
doy pack
Heatable pot
Gourd
Etc.
CATEGORY
flexible
rigid
reheatable
printed
storage before use
Etc.
POLYMER
PS
PA
PVDC
acrylic adhesive
aluminum
nitro ink
SUBSTANCE
Technolofical function
chemical function
IUPAC
CAS
M range
Etc.
FOOD STORAGE
frozen
chilled
hot filled
Microwave heating
Sterilized
SAFEFOODPACK DESIGN
olivier.vitrac@agroparistech.fr
Sept 2015
INRA
SCIENCE & IMPACT
.041
Sept 2015

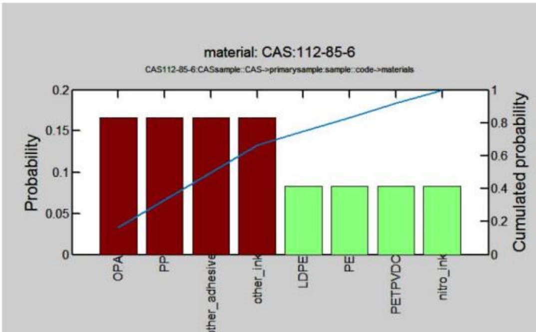
EXAMPLES

WHICH MATERIAL TO BE USED TO STORE MILK IN "GOURD"



EVOH	ethylene vinyl alcohol
PE	polyethylene
PP	polypropylene
HDPE	high density polyethylene

WHICH MATERIAL MAY CONTAIN THIS SUBSTANCE?



OPA	oriented polyamide
PP	polypropylene
other_adhesive	others adhesives
other_ink	others inks, no specifically defined
LDPE	low density polyethylene
PE	polyethylene
PETPVDC	PVDC coated polyethyleneterephthalate
nitro_ink	nitrocellulosic ink

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SafeFoodPack Design

.043
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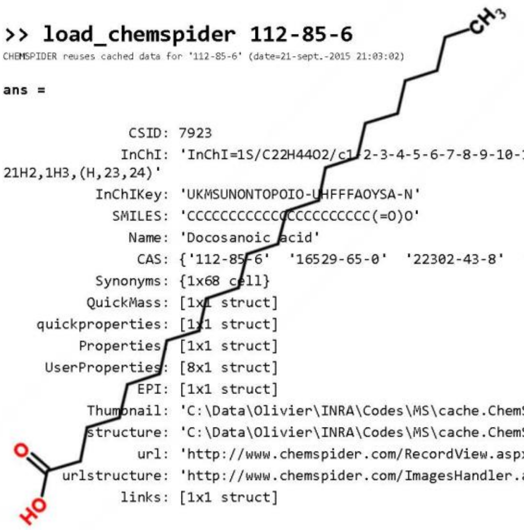
EXAMPLES

WHAT IS THIS 112-85-6 ?

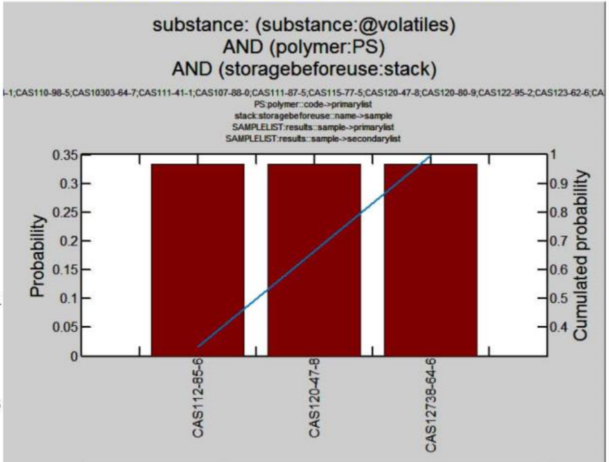



```
>> load_chemspider 112-85-6
CHEMSPIDER reuses cached data for '112-85-6' (date=21-sept.-2015 21:03:02)

ans =

           CSID: 7923
          InChI: 'InChI=1S/C22H44O2/c1-2-3-4-5-6-7-8-9-10-11-1
21H2,1H3,(H,23,24)'
       InChIKey: 'UKMSUNONTOPOIO-UHFFFAOYSA-N'
         SMILES: 'CCCCCCCCCCCCCCCCCCCCCC(=O)O'
           Name: 'Docosanoic acid'
            CAS: {'112-85-6'  '16529-65-0'  '22302-43-8'  '505
       Synonyms: {1x68 cell}
      QuickMass: [1x1 struct]
quickproperties: [1x1 struct]
     Properties: [1x1 struct]
 UserProperties: [8x1 struct]
            EPI: [1x1 struct]
      Thumbnail: 'C:\Data\Olivier\INRA\Codes\MS\cache.ChemSpid
      structure: 'C:\Data\Olivier\INRA\Codes\MS\cache.ChemSpid
            url: 'http://www.chemspider.com/RecordView.aspx?id
   urlstructure: 'http://www.chemspider.com/ImagesHandler.ashx
          links: [1x1 struct]
```

VOLATILE MIGRANTS FROM PS STORED BEFORE USE AS STACKS?

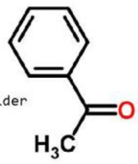


CAS112-85-6	Docosanoic acid
CAS120-47-8	4-(2-Aminoethyl)aniline
CAS12738-64-6	+-D-Fructofuranosyl +-D-glucopyranoside

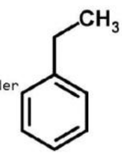
EXAMPLES OF PIPES

- ROUGH ESTIMATES OF A AIR/POLYMER PARTITION COEFFICIENTS

```
>> FMECAKairP acetophenone
LOAD_CHEMSPIDER        extraction of ChemSpiderID=7132 ('acetophenone') completed in 10.26 s
LOAD_CHEMISPIDER: updated cache
        7132.mat       21-sept.-2015 21:37:19      77.6 kBytes   C:\Data\Olivier\INRA\Codes\MS\cache.ChemSpider
CHEMSPIDER reuses cached data for 'acetophenone' (date=21-sept.-2015 21:37:19)
ans =
   9.1995e-06
```




```
>> FMECAKairP ethylbenzene
LOAD_CHEMSPIDER        extraction of ChemSpiderID=7219 ('ethylbenzene') completed in 11.9 s
LOAD_CHEMISPIDER: updated cache
        7219.mat       21-sept.-2015 21:42:34      107.1 kBytes   C:\Data\Olivier\INRA\Codes\MS\cache.ChemSpider
CHEMSPIDER reuses cached data for 'ethylbenzene' (date=21-sept.-2015 21:42:34)
ans =
   2.2485e-04
```




```
>> FMECAKairP 'benzoic acid'
LOAD_CHEMSPIDER        extraction of ChemSpiderID=238 ('benzoic acid') completed in 5.746 s
LOAD_CHEMISPIDER: updated cache
        238.mat        21-sept.-2015 21:45:01      41.2 kBytes   C:\Data\Olivier\INRA\Codes\MS\cache.ChemSpider
CHEMSPIDER reuses cached data for 'benzoic acid' (date=21-sept.-2015 21:45:01)
ans =
   1.3674e-08
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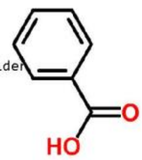
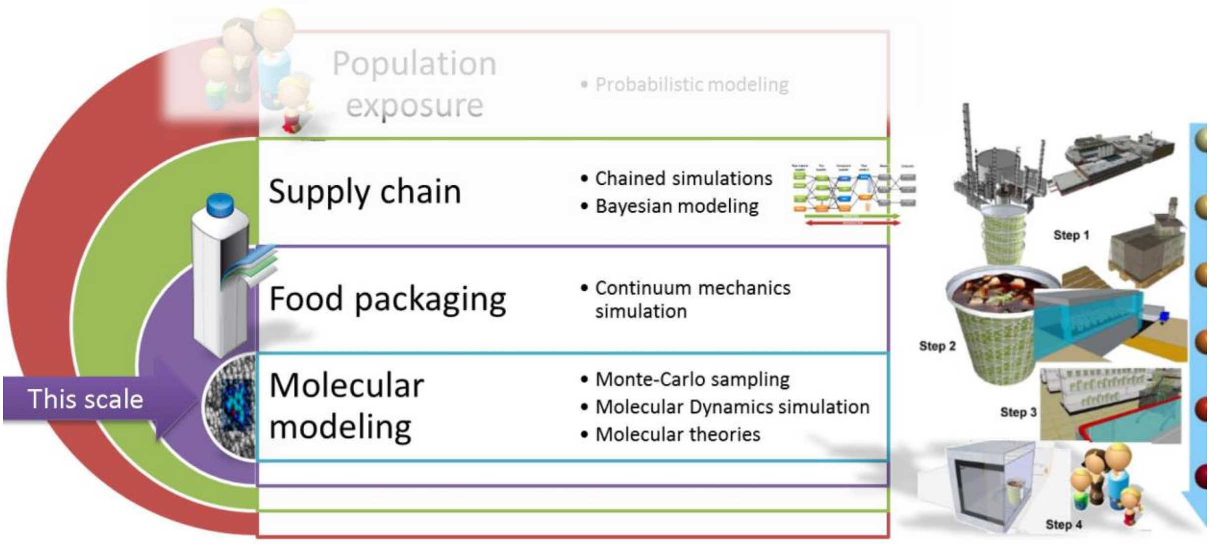


_04

MOLECULAR MODELING

PREDICTING DIFFUSION COEFFICIENTS

NESTED MODELING HIERARCHY



Systems Analysis at the Molecular Scale

HERSCHEL RABITZ

Problems involving physiochemical phenomena on both the microscopic and macroscopic scales often raise similar sets of generic issues and questions. The complexity of these problems is beginning to make inoperative the traditional intuition-based approaches to their analysis and solution. The common characteristics of large, multivariable, complex molecular systems call for a new, more systematic approach to guide theoretical and experimental efforts. With mathematical modeling becoming an essential ingredient in the studies, it is argued that molecular systems analysis and especially the systematic tools of sensitivity analysis can play an increasingly important role in understanding and finding solutions to complex, chemically based problems.

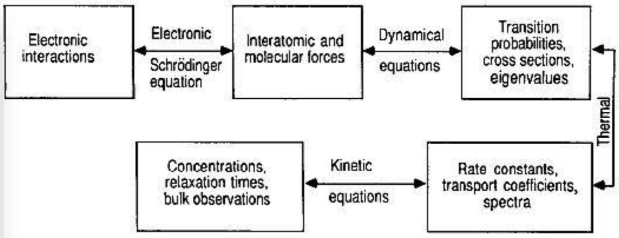
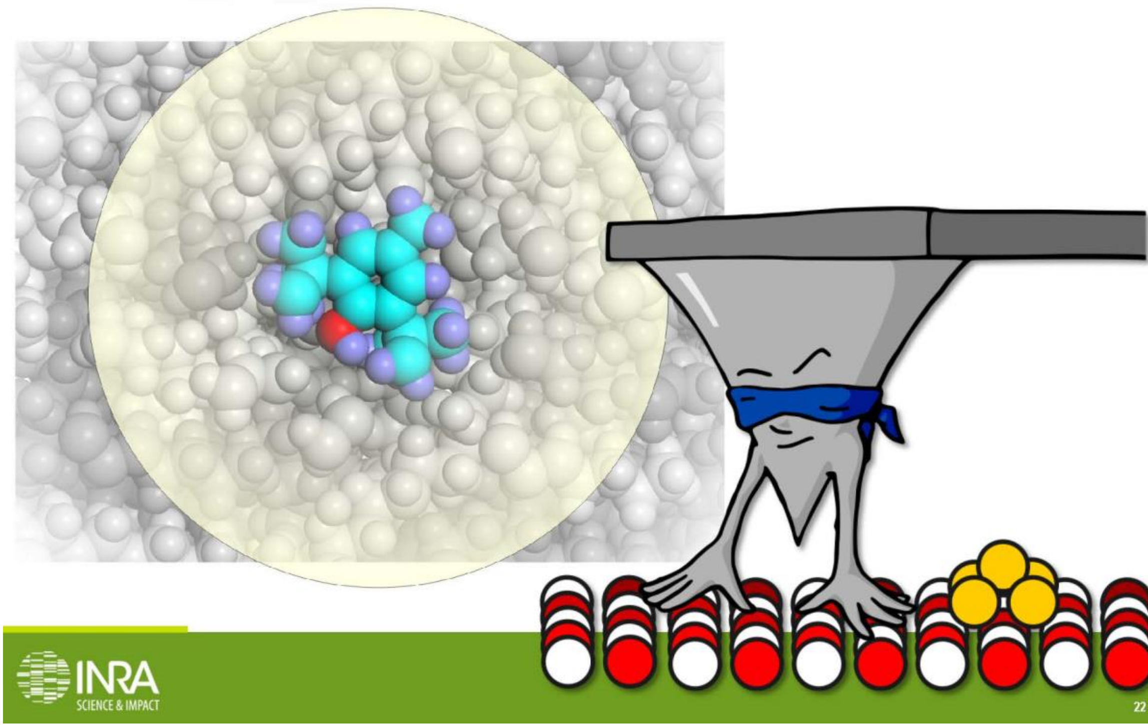


Fig. 1. Flow chart illustrating the hierarchical connection between microscopic and macroscopic variables in chemical dynamics and kinetics. Sensitivity analysis techniques may be developed to specifically probe the parametric and functional interconnections between the levels of the flow chart. The double-headed arrows connecting elements in the flow chart imply that both forward and inverse questions may be explored.

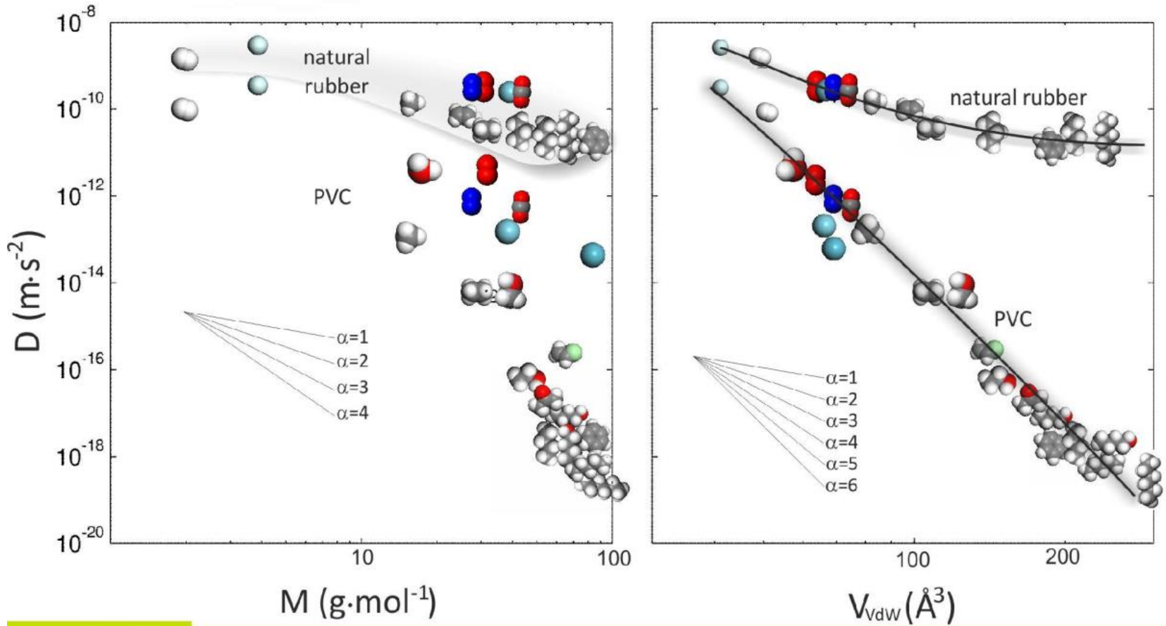
Science 13 October 1989:
Vol. 246 no. 4927 pp. 221-226

USING MOLECULAR MODELING AS A COMPUTATIONAL MICROSCOPE



SCALING D WITH SOLUTE SIZE

STIFF DIFFUSANTS



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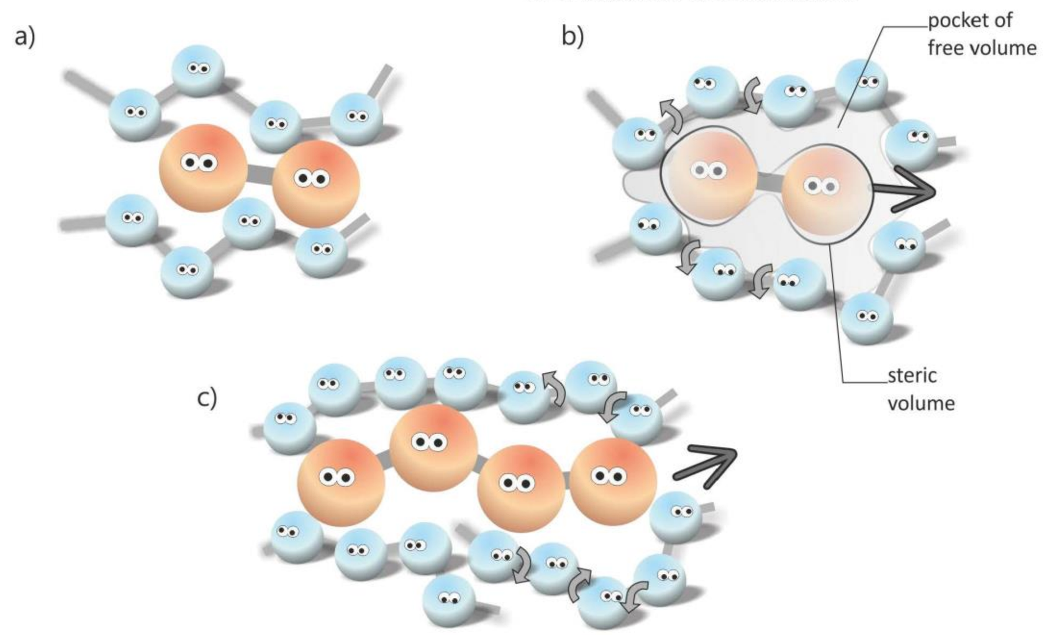
From: A. R. Berens, Pure Appl. Chem., **1981**, 53, 365

.050 Sept 2015

FLEXIBLE DIFFUSANTS

Local and temporary trapping of additive between polymer segments

Additive translation controlled by the relaxation of polymer itself and by the rate of creation of free volumes.



The relative free volume required for the translation of large additives is smaller as displacements of atoms/patterns are more likely not to be correlated together.

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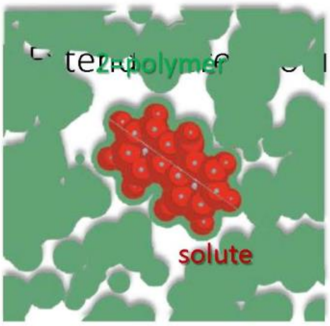
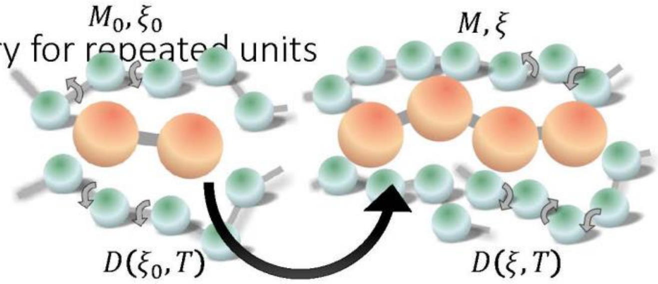
Extended free volume theory for repeated units





Solute geometry captured

by one single parameter $\xi = \frac{V_S^*}{V_m^*}$

Ratio of critical molar volume of solvent jumping unit to critical molar volume of polymer jumping unit

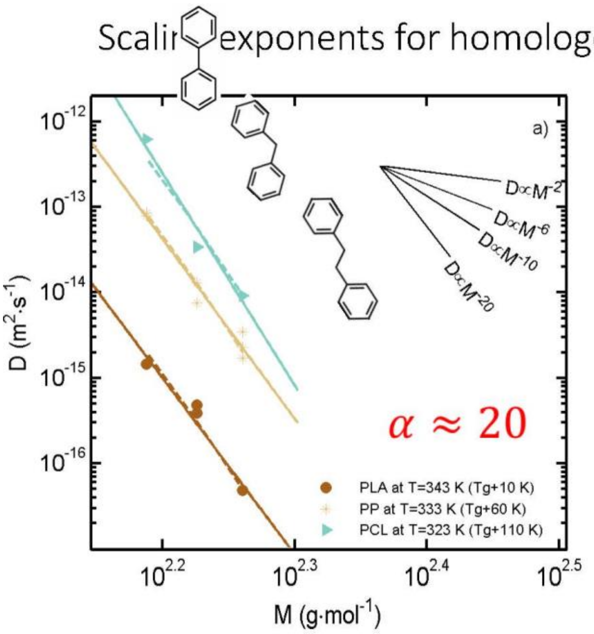
$$\frac{D(\xi,T)}{D(\xi_0,T)} = f\left(\frac{M}{M_0}\right) = g(exp[-(\xi-\xi_0)])$$

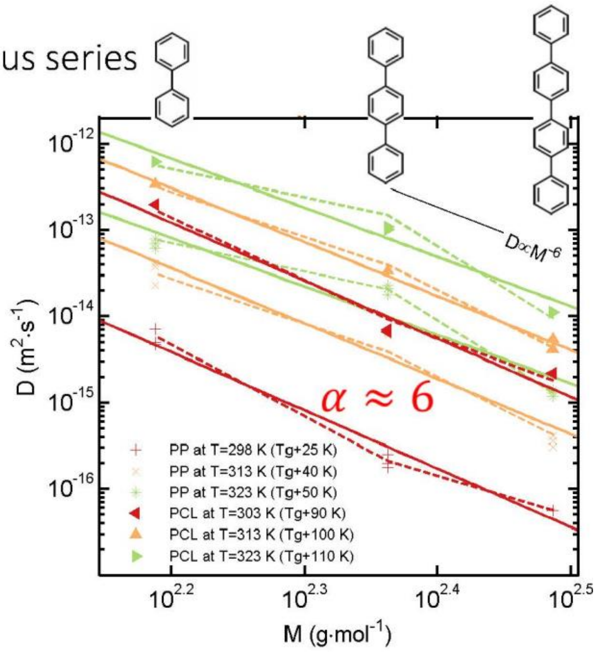
Eur. Polym. J. Vol. **34**, pp. 797, 1998
Macromolecules, Vol. **27**, pp. 4684, 1994

From Vrentas et al. **(1977, 1996, 1998) theory, trace diffusion coefficient ratio can be expressed as:**

T>Tg
$$\frac{D(\xi,T)}{D(\xi_0,T)} = \exp\left(-\frac{E^*(\xi)-E^*(\xi_0)}{RT}\right)\exp\left(-(\xi-\xi_0)\frac{\gamma_2\tilde{V}_2^*}{K_{12}(K_{22}+T-Tg)}\right)$$

Scaling exponents for homologous series

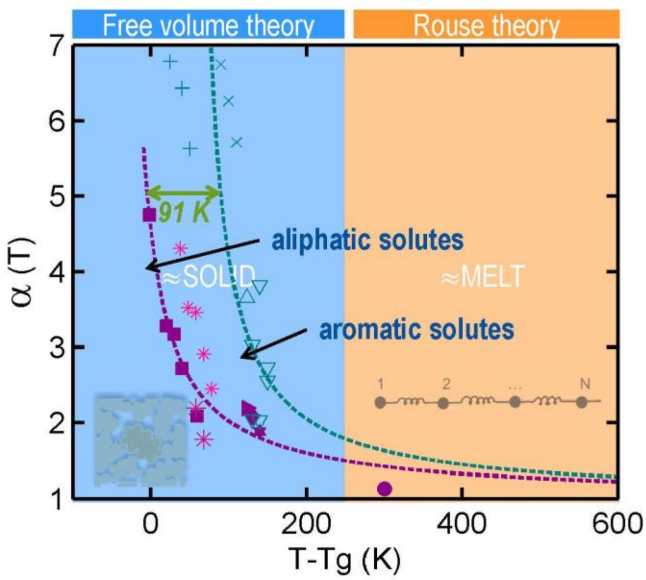


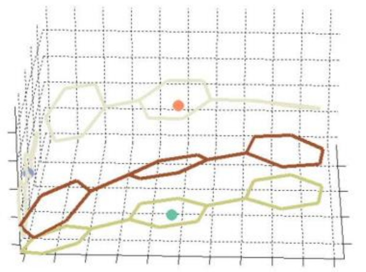


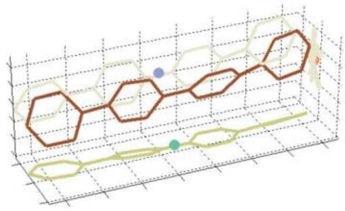
$$\alpha = \left.\frac{\partial lnD}{\partial lnM}\right|_{M_0,T,Tg} \gg 1$$

SCALING EXPONENTS

FOR HOMOLEGOUS SERIES OF SUBSTANCES







$$\alpha\left(T-Tg\right)=1+\frac{K_{\alpha}}{T-Tg+K_{\beta}}$$

Blob Shape/size

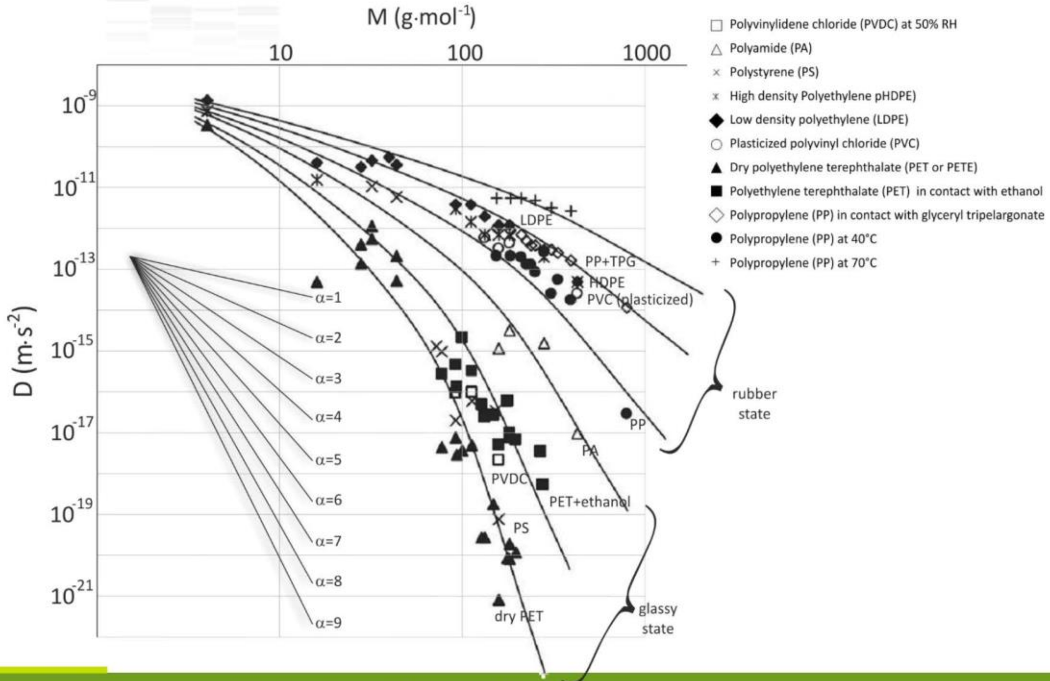
Formal equivalences between FVT and scaling laws

Rubber polymers: $T > T_g$

	Scaling law (Eq. (19))	*Free-volume theory (Eq. (22))*
Relative diffusant effects	$\ln\left(\frac{M}{M_0}\right)$	$0.24\left(\xi-\xi_0\right)$
Scaling exponent $\alpha(T,Tg)$	$1+\frac{K_\alpha}{T-T_g+K_\beta}$	$0.24\frac{\gamma}{K_{12}}\frac{\hat{V}_P^*}{K_{22}+T-T_g}$ K_{12}, K_{22} are polymer free-volume parameters.
Relative activation energy $Ea\left(M,T\right)-Ea\left(M_0,T\right)=$ $Ea\left(\xi,T\right)-Ea\left(\xi_0,T\right)=$ $\frac{\partial\ln\frac{D(M,T)}{D(M_0,T)}}{\partial 1/T}=$	$K_\alpha\frac{RT^2}{\left(T-T_g+K_\beta\right)^2}\ln\frac{M}{M_0}$	$\underbrace{E^*\left(\xi\right)-E^*\left(\xi_0\right)}_{\to 0}$ $+\left(\xi-\xi_0\right)\frac{\gamma\bar{V}_P^*}{K_{12}}\frac{RT^2}{\left(K_{22}+T-T_g\right)^2}$

SCALING EXPONENTS

FOR VARIOUS POLYMERS



Crit. Rev. Food Sci. Nut. 2015 (Fang & Vitrac)

http://www.tandfonline.com/doi/full/10.1080/10408398.2013.849654

INRA SCIENCE & IMPACT .056 Sept 2015

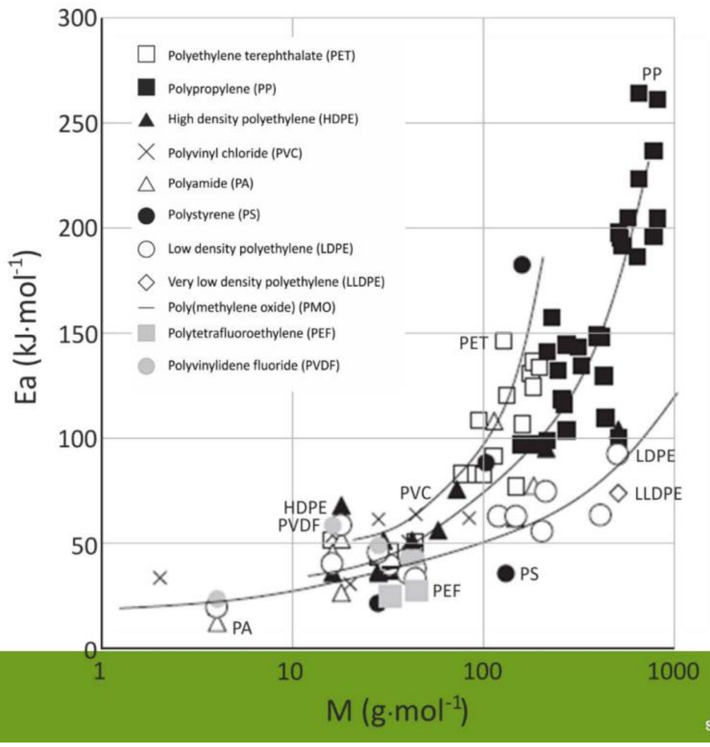
SCALING ACTIVATION ENERGY

VARIOUS DIFFUSANTS IN VARIOUS POLYMERS

$$\mathrm{Ea}(M) \approx \mathrm{Ea}(M_0) + ln(M/M_0)$$

Crit. Rev. Food Sci. Nut. 2015 (Fang & Vitrac)

http://www.tandfonline.com/doi/full/10.1080/10408398.2013.849654



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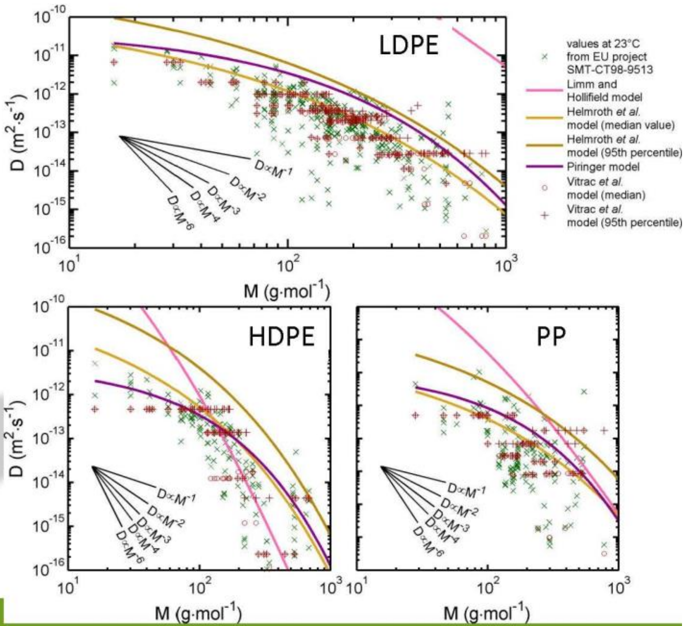
OVERESTIMATING D VALUES

PIRGINGER EQUATION

$$\ln\breve{D}_{(M,T)} = A'_P - 0.1351M^{2/3} + 0.003M - \frac{\tau + 10454}{RT}$$

SAFETY MARGIN

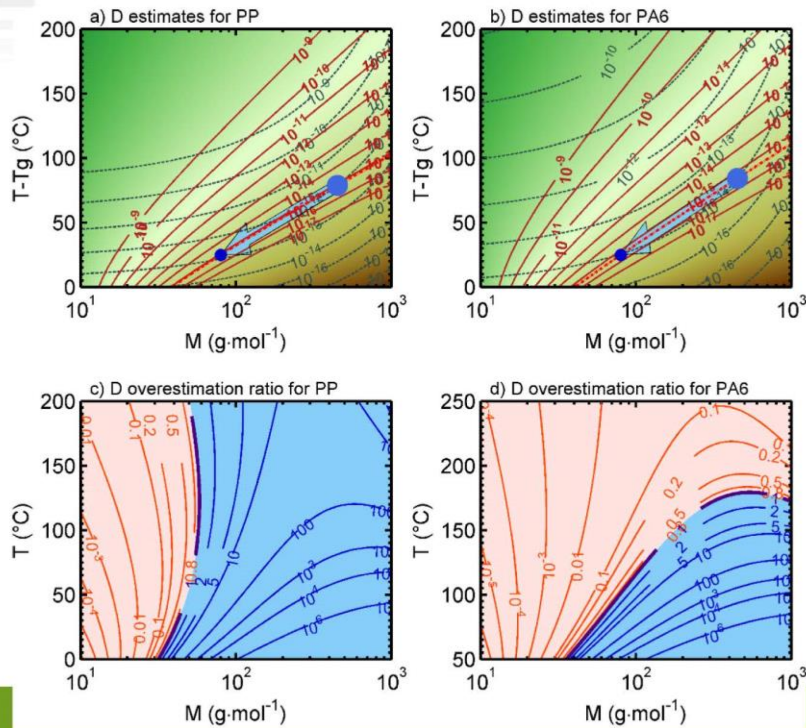
Polymer	A'_P	τ (K)
LDPE,LLDPE	11	0
HDPE	14	1565
PP (homo and random)	13	1565
PP (rubber)	11	0
PS	0	0
HIPS	1	0
PET	6	1565
PBT	6	1565
PEN	5	1565
PA	2	0
PVC	0	0



ROBUSTNESS OF THE PIRINGER EQUATION

RUBBER POLYMERS (T>Tg)

- Tg~0°C (PP)
- Tg~50°C (PA)



Crit. Rev. Food Sci. Nut. 2015 (Fang & Vitrac) http://www.tandfonline.com/doi/full/10.1080/10408398.2013.849654

_05

MOLECULAR MODELING

PARTITION AND ACTIVITY COEFFICIENTS

HEAT OF SORPTION/DESORPTION

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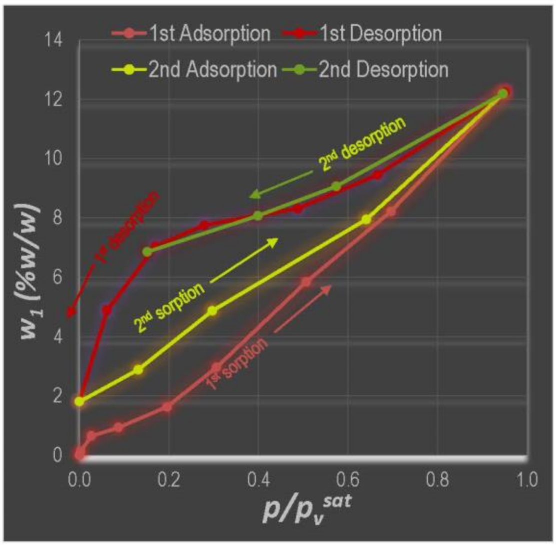
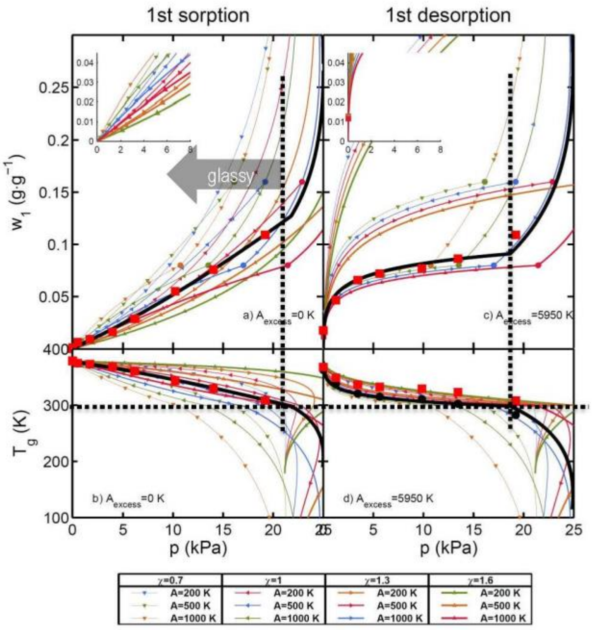
BEYOND PARTITION COEFFICIENTS

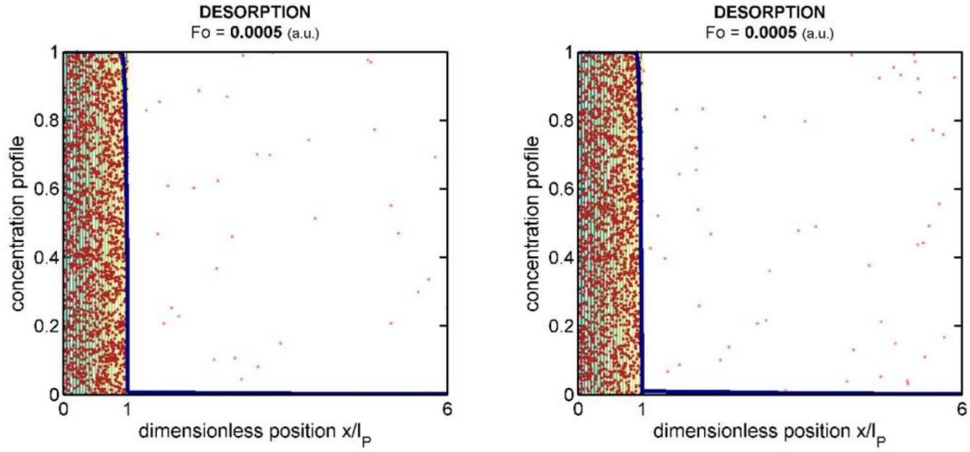
Sorption hysteresis of n-hexane in PS at 298 K





EFFECT OF PARTITION COEFFICIENT ON MIGRATION

	50 times for chemical affinity for P	50 times for chemical affinity for F
$K_{i,F/P}=$	1/50	50



$$K_{i,F/P}=\frac{C_{i,F}^{eq}}{C_{i,P}^{eq}}=\frac{1}{1-crystallinity}\frac{\gamma_{i,P_{amorphous}}^{v}}{\gamma_{i,F}^{v}}$$

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Sept 2015

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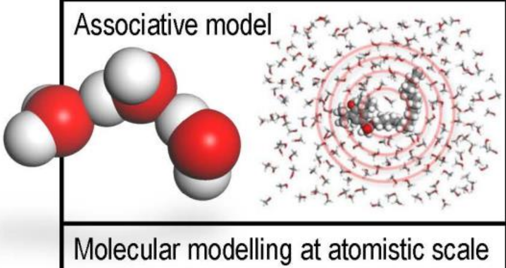
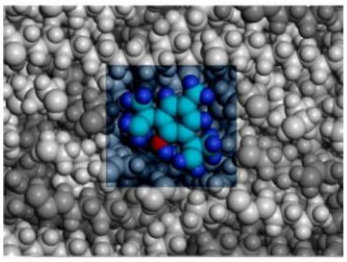
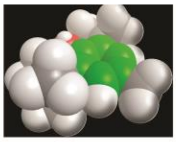
MANY METHODS AVAILABLE

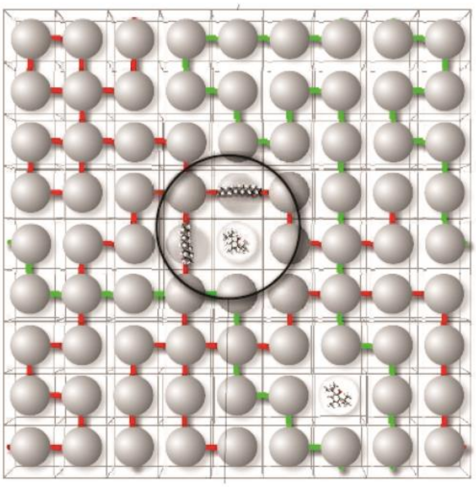
Class	Models
Group contribution	UNIQUAC, UNIFAC, NRTL
Associative model 	SAFT, PRISM Optimized for polar and liquid phase (De Anda et al Pol. Eng. & Sci., 2011)
Molecular modelling at atomistic scale 	Explicit representation of entangled chains Representation of polymer chains without entanglement

OFF-LATTICE FLORY-HUGGINS FORMULATION OF EXCESS CHEMICAL POTENTIALS IN **BINARY BLEND-VOID SYSTEMS**



Chemical potential (definition of J. Williard Gibbs)

$$\mu_{i,k}=\left(\frac{\partial G_{i+k}}{\partial n_i}\right)_{P,T,i\neq j}=\mu_i^0+RTlna_i=\mu_i^0+RTln\phi_i+RTln\gamma_{i,k}^v=\mu_i^0+\mu_i^{id}+\mu_{i,k}^{excess}$$



Flory expression at infinite dilution in k=P or in k=F

$$\frac{\left\{\mu_{i,k}^{excess}\right\}_{k=P,F}}{k_B\cdot T}=\ln\gamma_{i,k}^v=$$

$$\left(1-\frac{1}{r_k}\right)\cdot\phi_k+\chi_{i,k}\cdot\phi_k^2\approx\left(1-\frac{1}{r_k}\right)+\chi_{i,k}$$

$$2k_BT\chi_{i,k}=\langle h_{i+k}\rangle_T+\langle h_{k+i}\rangle_T-\langle h_{k+k}\rangle_T-\langle h_{i+i}\rangle_T$$

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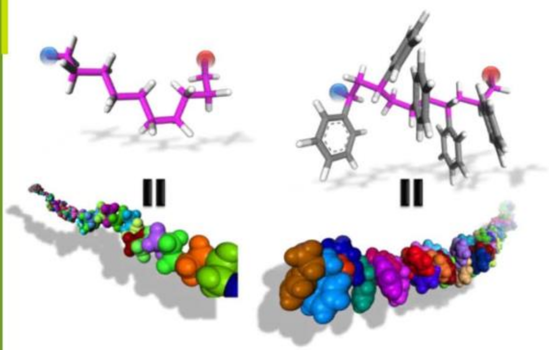
$$\ln\left(\gamma_{i,k}^v\right)=\left(1-\frac{1}{r_k}\right)\phi_k+\chi_{i,k}\phi_k^2$$

$$k=P,F$$

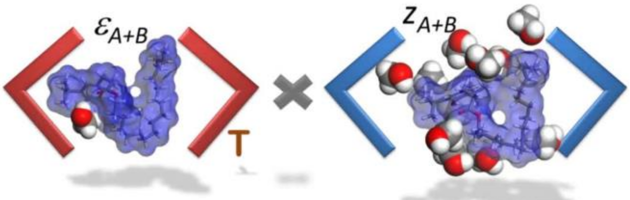
FLORY HUGGINS APPROXIMATION AT ATOMISTIC SCALE



IDEALIZED POLYMER CHAINS ($k=P$)

$$2k_BT\chi_{i,k}=\langle h_{i+k}\rangle_T+\langle h_{k+i}\rangle_T-\langle h_{k+k}\rangle_T-\langle h_{i+i}\rangle_T$$

EXCESS ENTHALPIES ARE CALCULATED FROM SIMPLE A MIXING RULE OF PAIR CONTACT ENERGIES



$$\langle h_{A+B}\rangle_T=\langle\varepsilon_{A+B}z_{A+B}\rangle_T\approx\langle\varepsilon_{A+B}\rangle_T\langle z_{A+B}\rangle$$

Bawendi et al., *J. Chem Phys.* 1986; 1987; 1988

Gillet et al., *I&EC*, 2009; 2010 ; Vitrac and Gilet, *Int. J. Chem. Reactor Eng.* 2010

SAFEFOODPACK DESIGN

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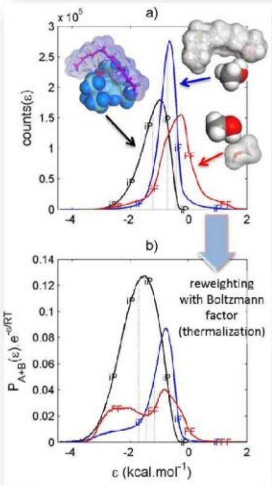
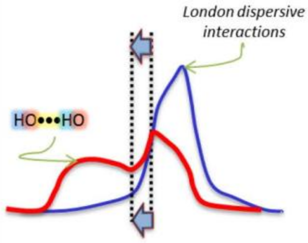
DETAILS OF THE ENERGY SAMPLING PROCEDURE

Pair contact energies



$$\langle \varepsilon_{A+B} \rangle_T = \frac{\int_{-\infty}^{+\infty} \varepsilon pr(\varepsilon) \exp\left(-\frac{\varepsilon}{RT}\right) d\varepsilon}{\int_{-\infty}^{+\infty} pr(\varepsilon) \exp\left(-\frac{\varepsilon}{RT}\right) d\varepsilon}$$



Excess enthalpies

Homopolymers

- $\chi_{i,P}^{\left(n_{i,P}^{\min}\right)} = \frac{\langle h_{i+P}^{n_{i,P}^{\min}} \rangle_T + \langle h_{P+i}^{n_{i,P}^{\min}} \rangle_T - \langle h_{P+P}^{n_{i,P}^{\min}} \rangle_T - \langle h_{i+i} \rangle_T}{2RT}$
- $n_{i,P}^{\min} = \underset{n_P}{\operatorname{argmin}} \left(\chi_{i,P}^{(n_P)}\right)$
- $\langle h_{j+k} \rangle_T = \langle \epsilon_{j+k} \rangle_T \langle z_{j+k} \rangle + \beta_{jk}$

In liquids (denoted F ou L)

- $\chi_{i,F} = \frac{\langle h_{i+F} \rangle_T + \langle h_{F+i} \rangle_T - \langle h_{F+F} \rangle_T - \langle h_{i+i} \rangle_T}{2RT}$
- For water: $\langle h_{F+F} \rangle_T = 4 \langle \varepsilon_{A+B} \rangle_T \langle z_{A+B} \rangle$

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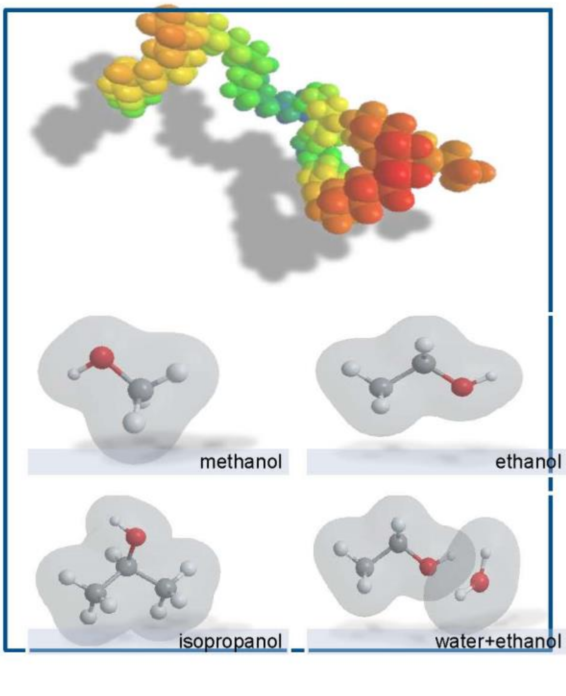
FIRST COMPARISONS BETWEEN DIRECT CALUCLATIONS AND EXPERIMENTS (no fit) – 45 SOLUTES

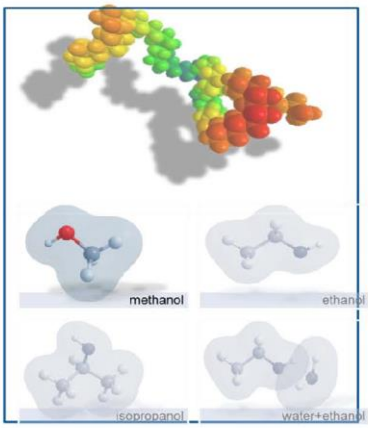
Polyethylene in contact with

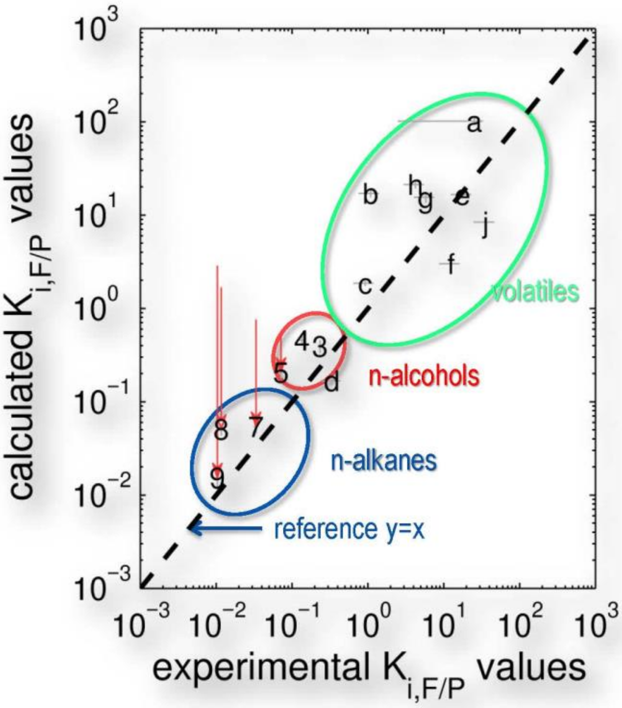


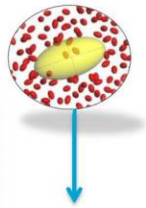
Alkanes	Alcohols	Volatiles	Plastics additives
decane	decanol	camphor	BHT
undecane	undecanol	diphenyl oxide	chimassorb 81
dodecane	dodecanol	diphenylmethane	Erucamide
tridecane	tridecanol	d-limonene	Irganox 1076
tetradecane	tetradecanol	dl-menthol	Irganox 1035
pentadecane	pentadecanol	eugenol	Irganox 245
hexadecane	hexadecanol	isoamyl acetate	Irgafos 168
heptadecane	heptadecanol	linalyl acetate	Irganox 3114
octadecane	octadecanol	phenylethyl alcohol	Irganox ps802
nonadecane	nonadecanol		stearic acid
eicosane	eicosanol		Tinuvin 326
docosane			
tetracosane			
octacosane			

67

METHANOL-POLYETHYLNE PARTITIONING







Effect of overlapping F molecules

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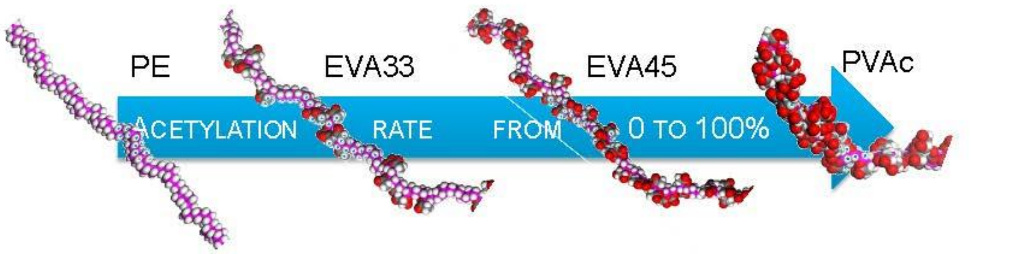
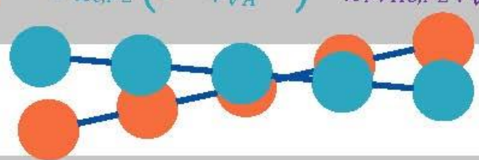
EXTENSION TO COPOLYMERS (ethylene vinyl acetate)



APOLAR POLARITY++

Mean field approximation (Flory-Huggins ternary : *i* + PE + PVAc)

$$\chi_{i,EVA}^{(w_{VA})} = \chi_{i,PVAc}\phi_{VA}^{(w_{VA})} + \chi_{i,PE}\left(1-\phi_{VA}^{(w_{VA})}\right) - \chi_{PVAc,PE}\phi_{VA}^{(w_{VA})}\left(1-\phi_{VA}^{(w_{VA})}\right)$$



Microscopic approach (binary : *i* + copolymer) : sampling of all possible isomers

MACROSCOPIC VS MICROSCOPIC MIXING ENERGIES

Polymer Blends

- $$\Delta\mu_i^{ex} = \frac{1}{RT}\frac{\partial \Delta_{mix}G}{\partial N_i}\Big|_{\{N_k\}_{k=1..\nu},T,P} - \ln(\phi_i) = \sum_{k=1..\nu}\left(1-\frac{r_i}{r_k}\right)\phi_k + r_i \sum_{j=1..\nu}\chi_{ij}\phi_j^2 + r_i \sum_{\substack{j=1..\nu\\k=1..\nu\\j<k}} (\chi_{ij}+\chi_{ik}-\chi_{jk})\phi_j\phi_k$$

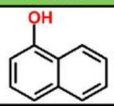
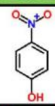
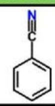
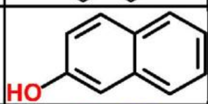
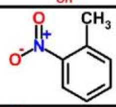
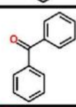
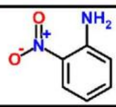
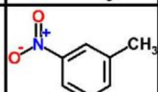
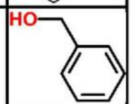
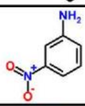
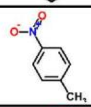
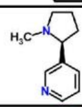
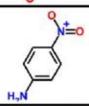
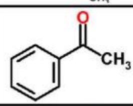
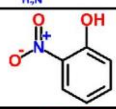
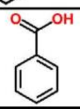
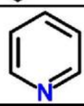
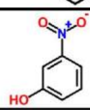
- For binary systems:
  $$\chi_P = \frac{1}{2}(\chi_{i1}+\chi_{i2}-\chi_{12})$$

Random copolymers, block polymers

- $$\chi_P = \sum_{k=1..\nu} \frac{p_{ii}p_{ik}h_{ik} + p_{ii}p_{ki}h_{ki} - p_{ii}p_{ik}h_{ii} - p_{ii}p_{ki}h_{kk}}{(p_{ii}+p_{ii})k_BT} - \sum_{\substack{j=1..\nu\\k=1..\nu\\j<k}} p_{ij}p_{ik}\chi_{jk} = \sum_{k=1..\nu} p_{ik}\chi_{i,k} - \sum_{\substack{j=1..\nu\\k=1..\nu\\j<k}} p_{ij}p_{ik}\chi_{jk}$$

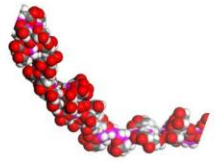
- $p_{ik} = p_{ki} = \phi_k$

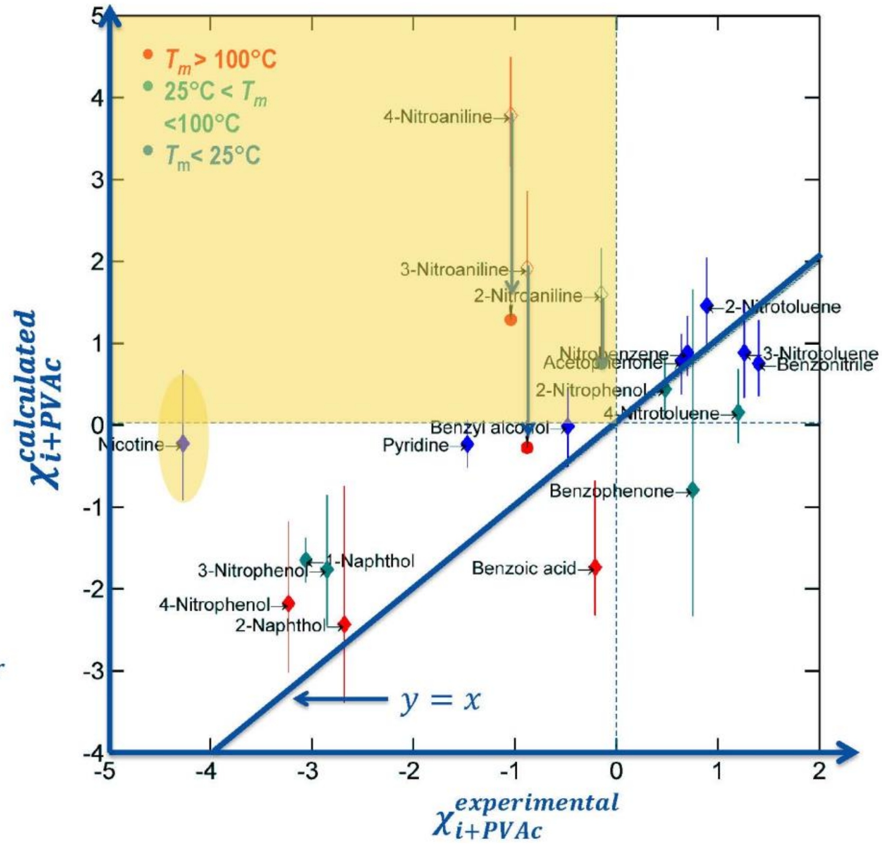
19 TESTED SOLUTES

Name	CAS number	Structure	Name	CAS number	Structure	Name	CAS number	Structure
1-Naphthol	1321-67-1		4-Nitrophenol	100-02-7		Benzonitrile	100-47-0	
2-Naphthol	135-19-3		2-Nitrotoluene	1321-12-6		Benzophenone	119-61-9	
2-Nitroaniline	29757-24-2		3-Nitrotoluene	1321-12-6		Benzyl alcohol	100-51-6	
3-Nitroaniline	99-09-2		4-Nitrotoluene	99-99-0		Nicotine	54-11-5	
4-Nitroaniline	100-01-6		Acetophenone	98-86-2		Nitrobenzene	98-95-3	
2-Nitrophenol	88-75-5		Benzoic acid	65-85-0		Pyridine	110-86-1	
3-Nitrophenol	554-84-7							

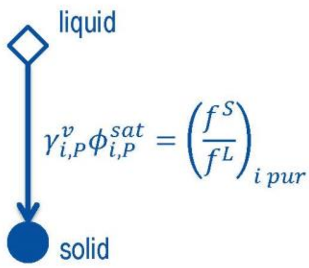
Reference data (group of Prausnitz): *J Appl Polym Sci* 2002, 85:2041–2052; *AIChE J* 2002, 48:1284-1291

VALUES OF χ FOR 19 SOLUTES IN HOMO-PVAC



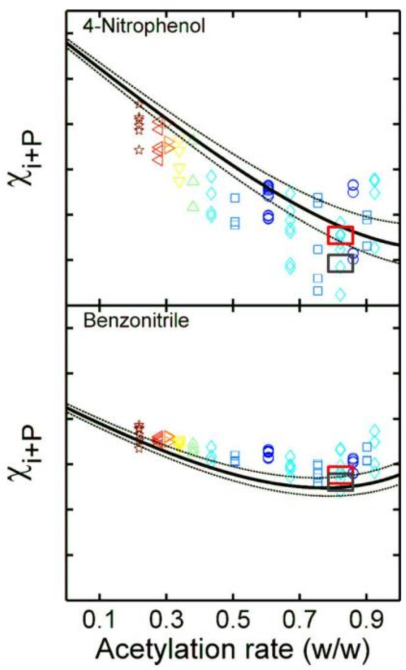


Solute reference state for expressing chemical potentials



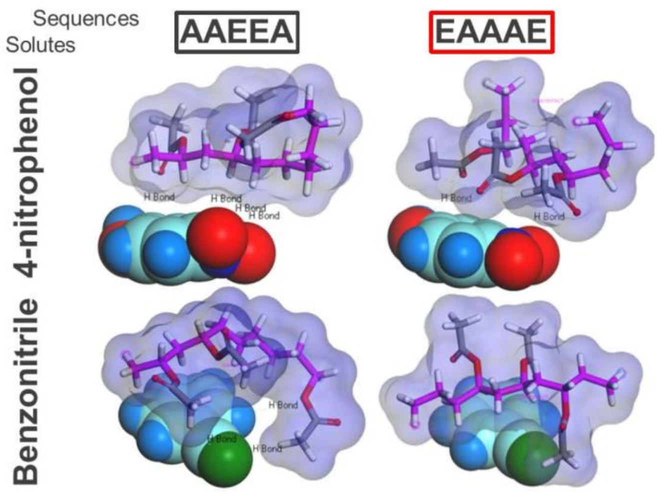
COMPARISON BETWEEN THE MICROSCOPIC AND MEAN FIELD APPROXIMATION

Effect of acetylation rate on χ



Configurations of minimal energies : $n = 5$

(acetylation rate w/w = 0.82)

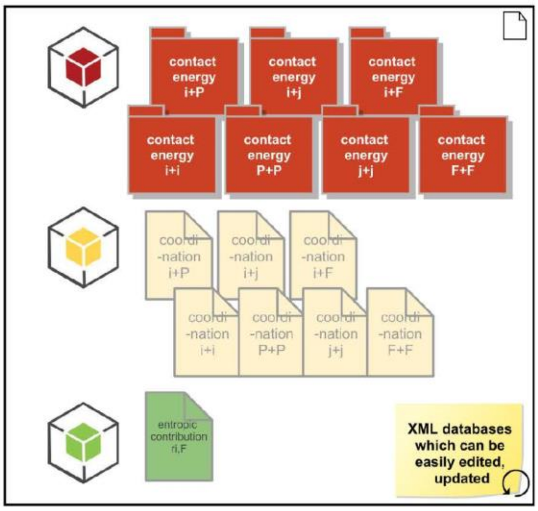


Microscopic calculations

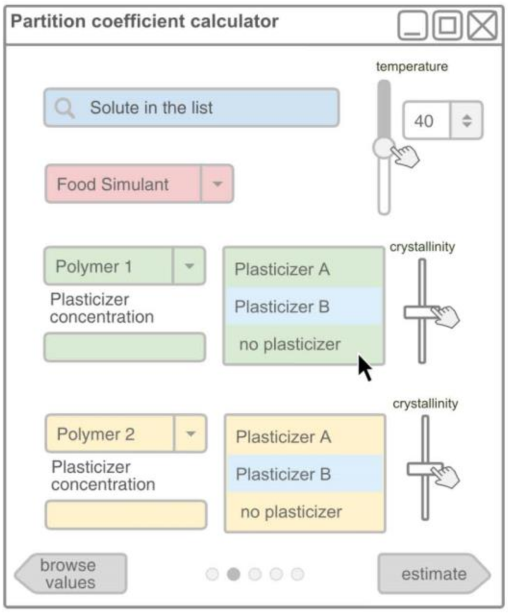
mean field approximation

MOLECULAR RESULTS INTEGRATED WITHIN A "SMALL" SOFTWARE

Databases of results calculated at *molecular scale*



Small "real-time" software



$i =$

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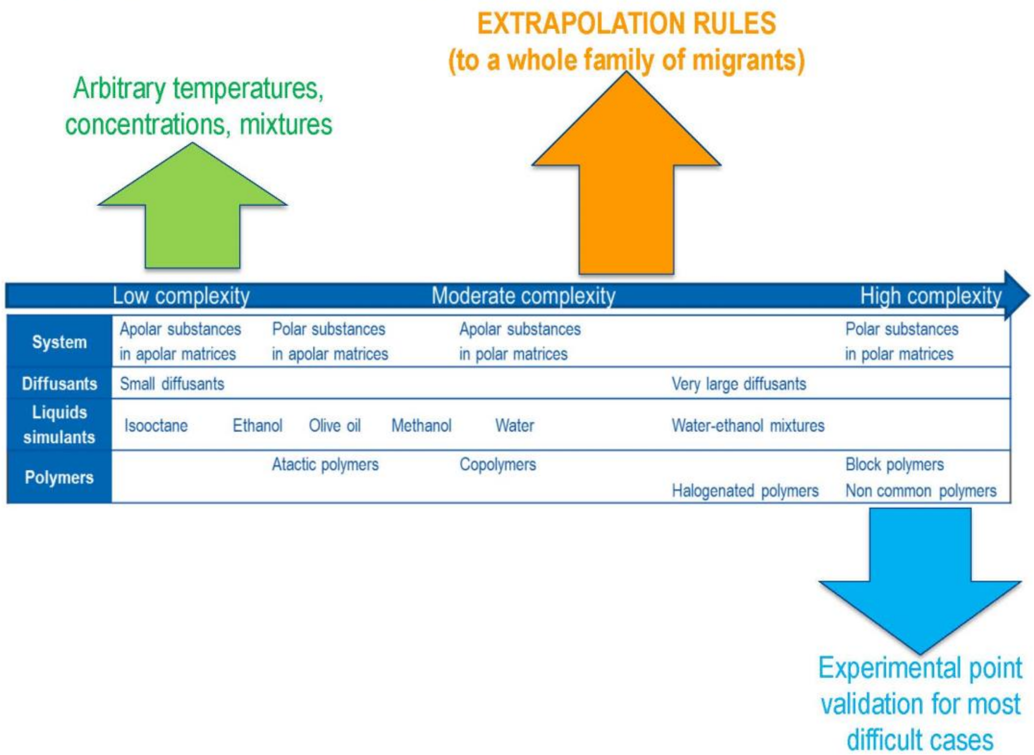
Which polymer? Which migrant? Which food simulant?

$i =$

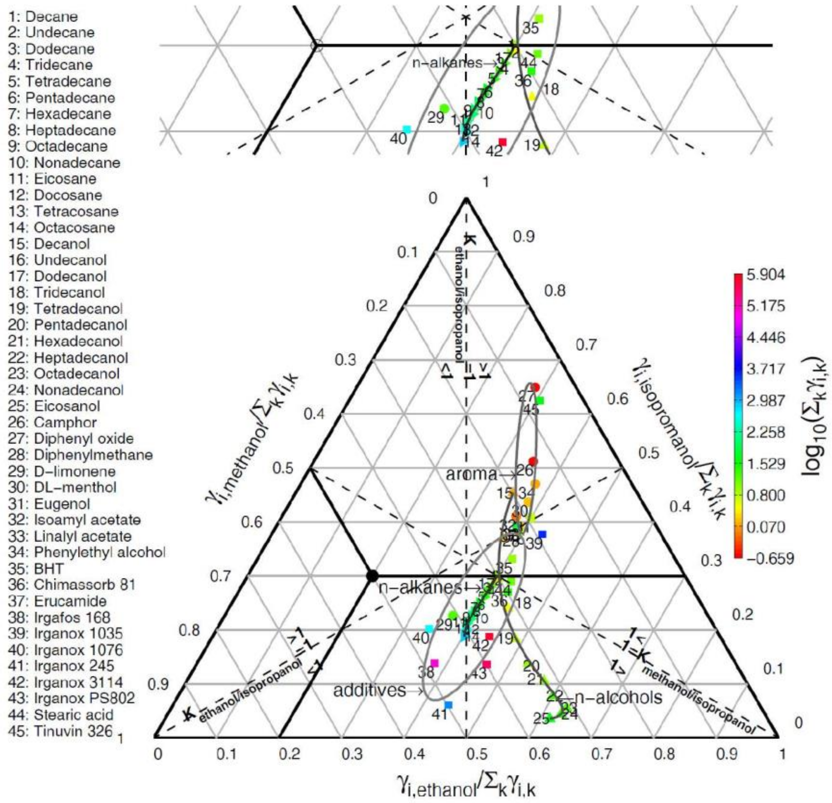


For 200 tabulated activity coefficients, one partition coefficient costs less than 1.5 € (with tax credit)

75

TOWARDS SIMPLE RULES

Vitrac, O. and G. Gillet (2010). "An Off-Lattice Flory-Huggins Approach of the Partitioning of Bulky Solutes between Polymers and Interacting Liquids." International Journal of Chemical Reactor Engineering 8.



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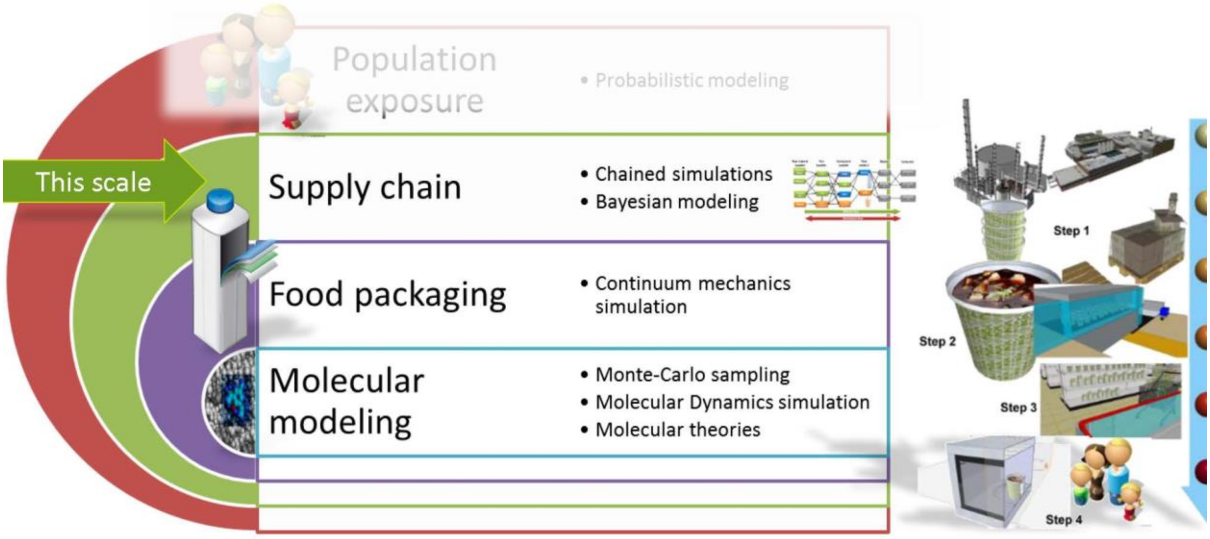
PREVENTIVE APPROACHES OF THE CONTAMINATION

FMECA APPROACHES

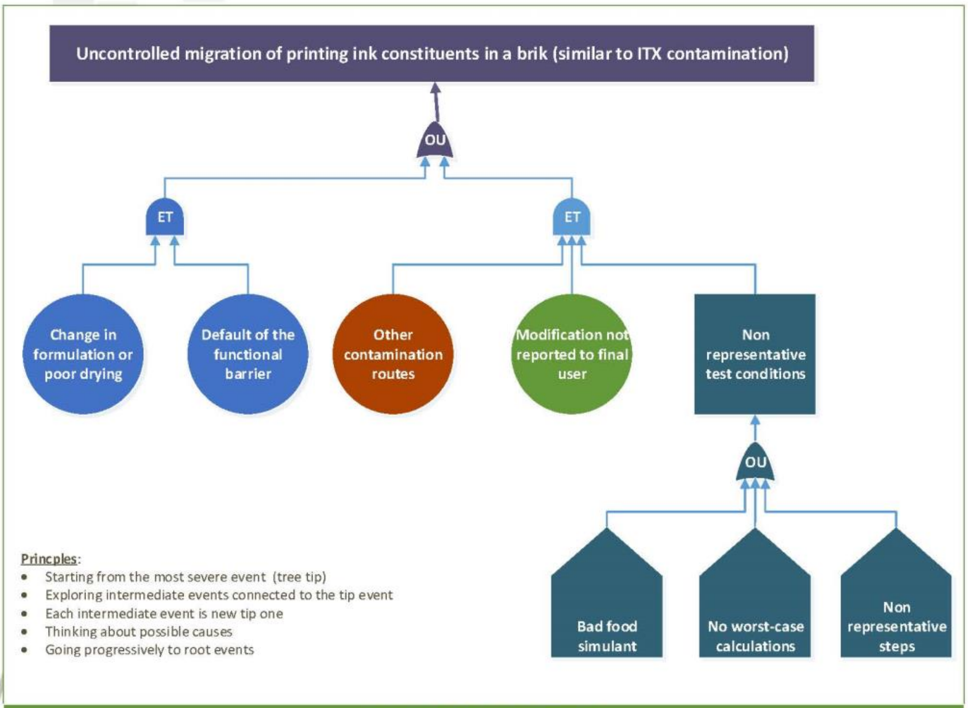
NESTED MODELING HIERARCHY



PREVENTIVE APPROACHES INSPIRED FROM AERONAUTICS INDUSTRY

Application to food packaging

Projet « Conception raisonnée d'emballages sûrs »

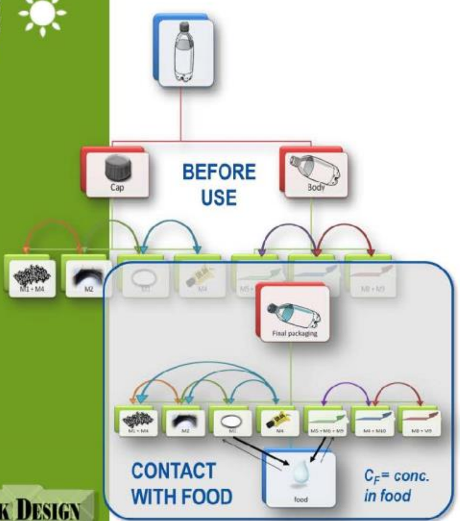


EXAMPLE OF A FAULT TREE

.080

Failure Mode Effects Criticality Analysis

LOGICAL STEPS



- List of components and functions
- Failure = migration mode tree
- **Severity** = $f(C_F)$
  - Dimensionless scale
  - Normalized by toxicological data
  - Substance and material independent
  - Linear to C_F for acceptable C_F values and non-linear beyond
- **Criticality ranking**
  - by component
  - by substance
  - by process or storage step
  - Comparative designs
- Ensuring **detectability** via calculations and simulation

Nguyen *et al.* 2013, AIChE J.

SAFEFOODPACK DESIGN

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Sept 2015

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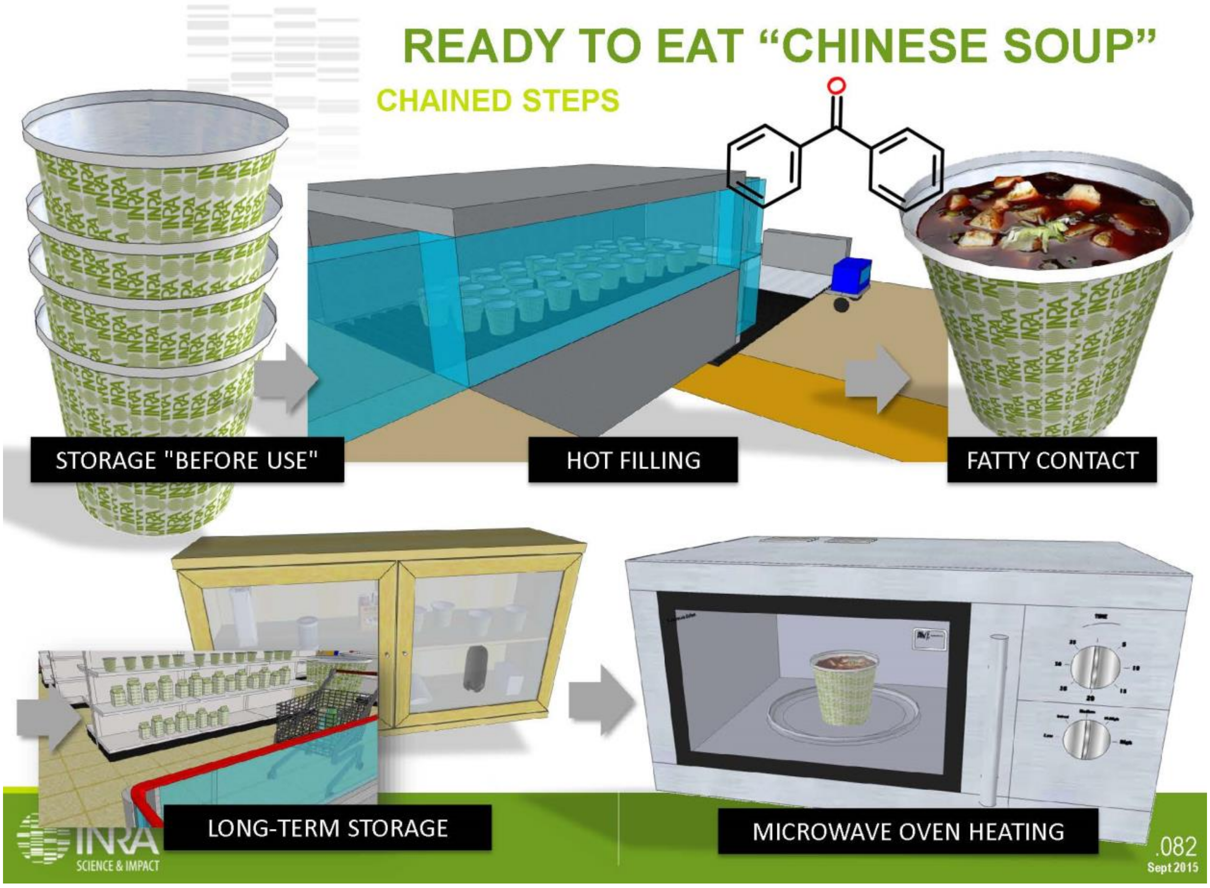
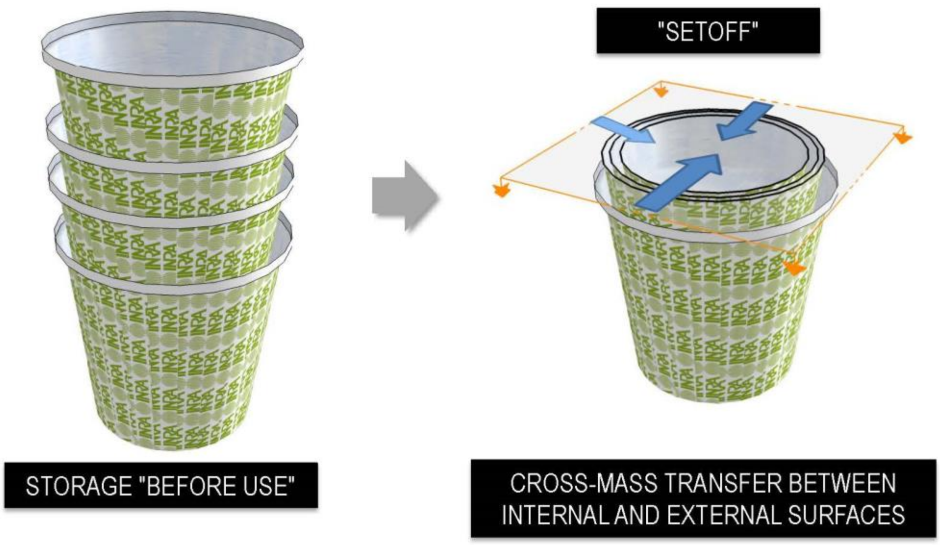


ALL STEPS MUST BE INCLUDED IN THE ANALYSIS

As soon they cause a redistribution of packaging constituents through the different materials (even without food contact).



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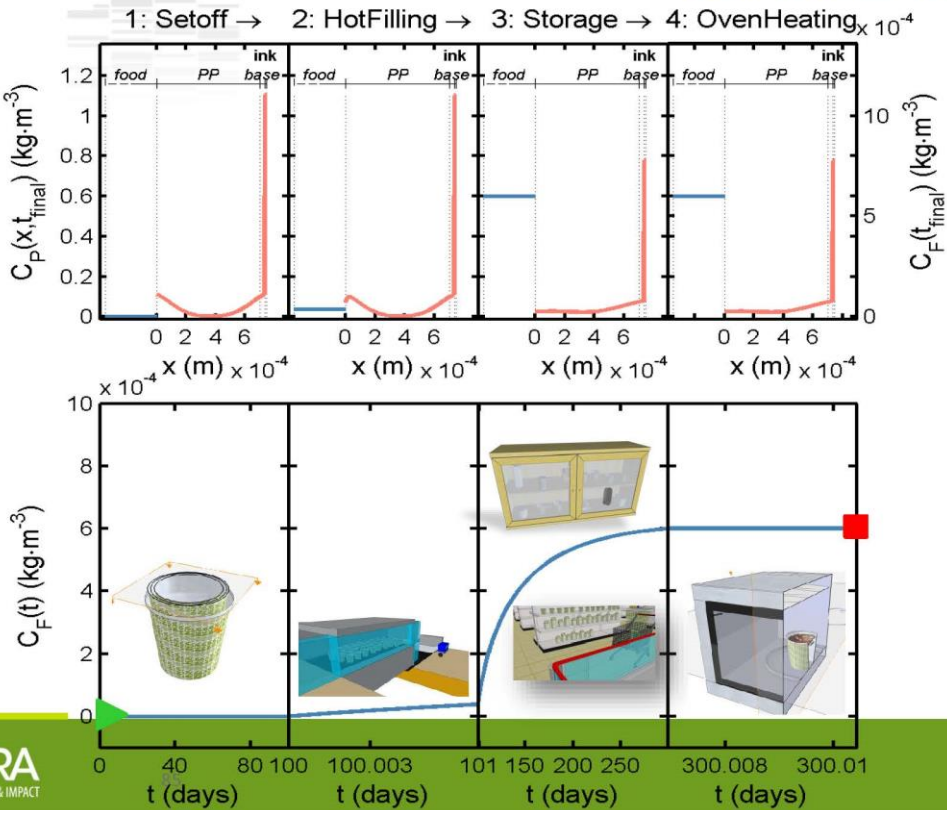
ALL STEPS MUST BE INCLUDED IN THE ANALYSIS

Mass transfer in the gas phase cannot be neglected during curing, long-term storage and oven heating

MICROWAVE HEATING

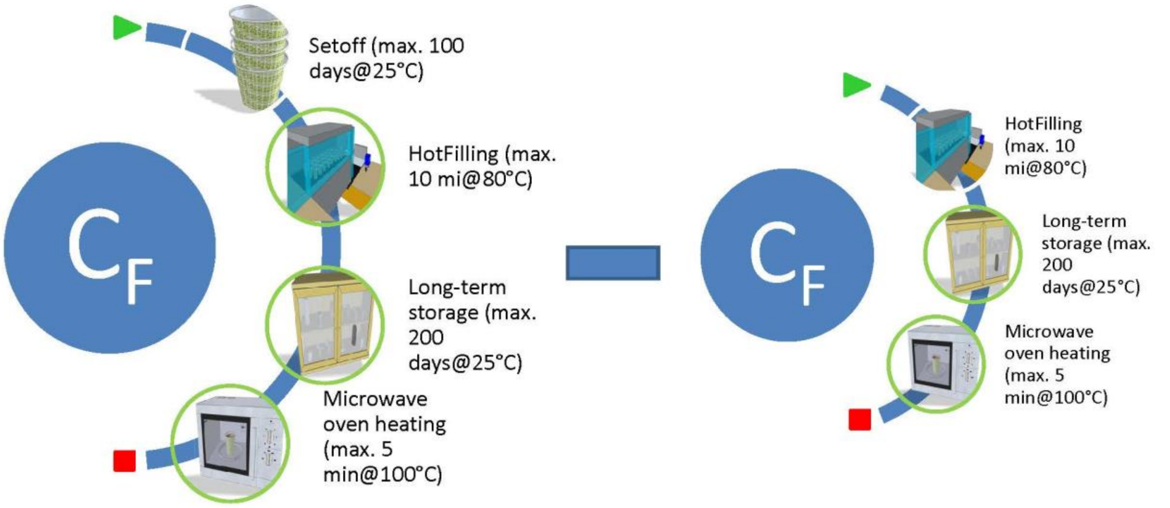
TRANSFER IN VAPOR PHASE
+STEAM EXTRACTION

CHAINED STEPS



ASSESSING THE SEVERITY OF A SINGLE STEP

CASE OF "SETOFF" STEP

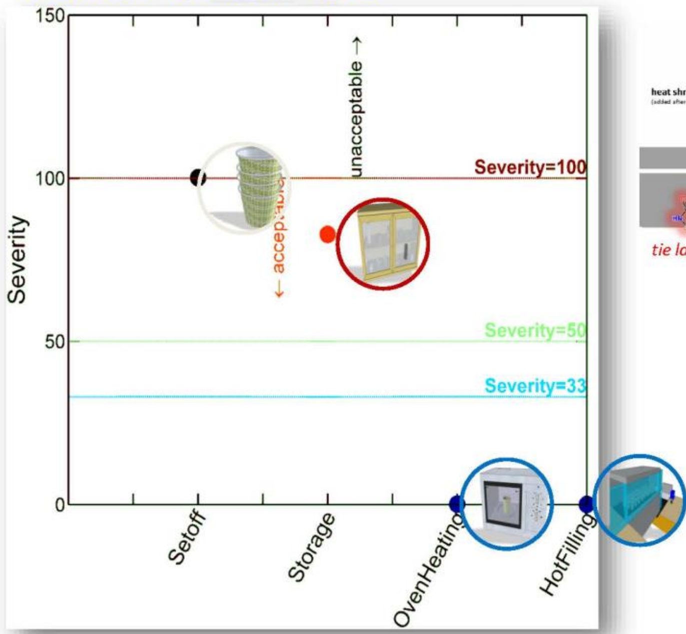


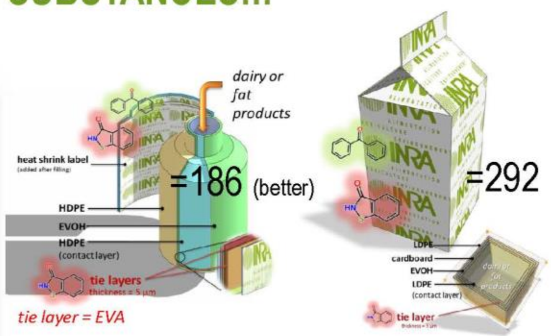
Full methodology described in *AIChE J.* 2013, **59**(4), 1183-1212

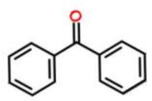
$$\mathrm{Severity}\left(\hat{C}_F\,(\mathrm{step}\,i)\right) = f\left(\max\left(\underbrace{C_{F_M}\Big|_{1\to2\to\cdots\to M} - C_{F_M}\Big|_{1\to2\to\cdots\to M/i}}_{\text{comparison with step } i \text{ removed}},\ \underbrace{C_{F_i}\Big|_i}_{\text{step } i \text{ alone}}\right)\right)$$

COMPARING THE SEVERITY OF A SEVERAL STEPS, PACKAGING DESIGNS, SUBSTANCES...

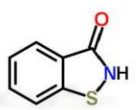
CASE OF "SETOFF" STEP







=115
(almost acceptable)



=124

Full methodology described in *AIChE J.* 2013, **59**(4), 1183-1212

Sept, 2015

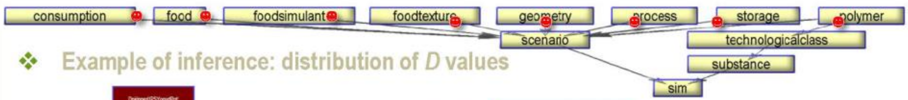
Food survey for non-experts in FCM

id	parent	geometry	polymer	food	foodsimulant	foodtexture	step	temperature	comment
LDPEYogurtBottle		smallbottle	LDPE	yogurt	ethanol50	liquid	storage	chilled	*pot of yogurt*
HDPEOilCap		cap	HDPE	oil	fatty	liquid	storage	ambient	*oil bottle cap*
PPDrinkGoblet		gobletPP	PP	hotdrink	ethanol50;fatty	liquid	consumption	hot	*coffee goblet*
PPButterContainer		container	PP	butter	fatty	semisolid	storage	chilled	*butter container*
PPCreamPot		container	PP	cream	fatty	semisolid	storage	chilled	*pot of cream*
PPDrinkStraw		straw	PP	yogurt	ethanol50	liquid	consumption	ambient	*straw*
PSYogurtPot		pot	PS	yogurt	ethanol50	semisolid	storage	chilled	*pot of yogurt*
PSDrinkGoblet		gobletPS	PS	hotdrink	ethanol50;fatty	liquid	consumption	hot	*coffee goblet*
PVCSauceLid		gasket	pPVC	sauce	fatty	liquid	process	sterilization	*cover gasket*
PVCSauceLid2	PVCSauceLid		pPVC	sauce	fatty	liquid	storage	ambient	

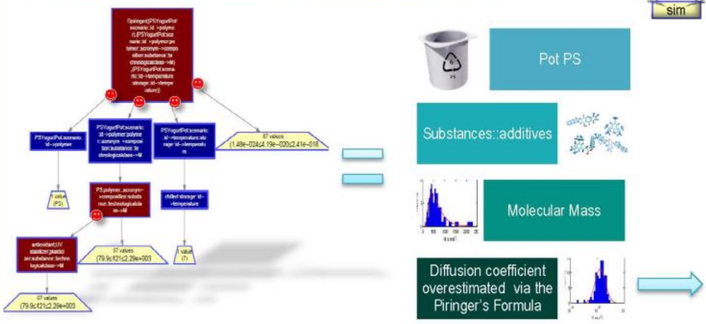
- 9 packaged food products purchased on the French market in 2011
- Geometry and materials were determined

id	parent	geometry	polymer	food	foodsimulant	foodtexture	step	temperature	comment
PSYogurtPot		pot	PS	yogurt	ethanol50	semisolid	storage	chilled	*pot of yogurt*

- Simulation scenarios were automatically generated via an expert system



- Example of inference: distribution of D values



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SafeFoodPack Design

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_07

GENERAL RECOMMENDATIONS

Training, education and cooperation programs

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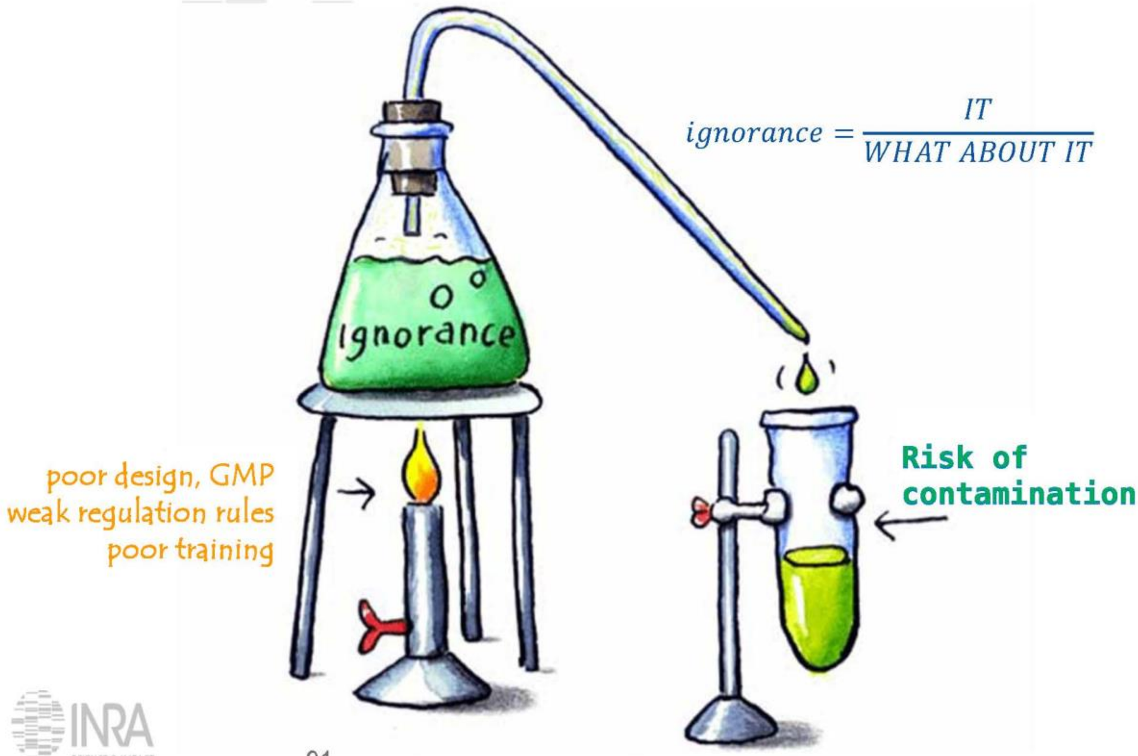
HUMAN RISK



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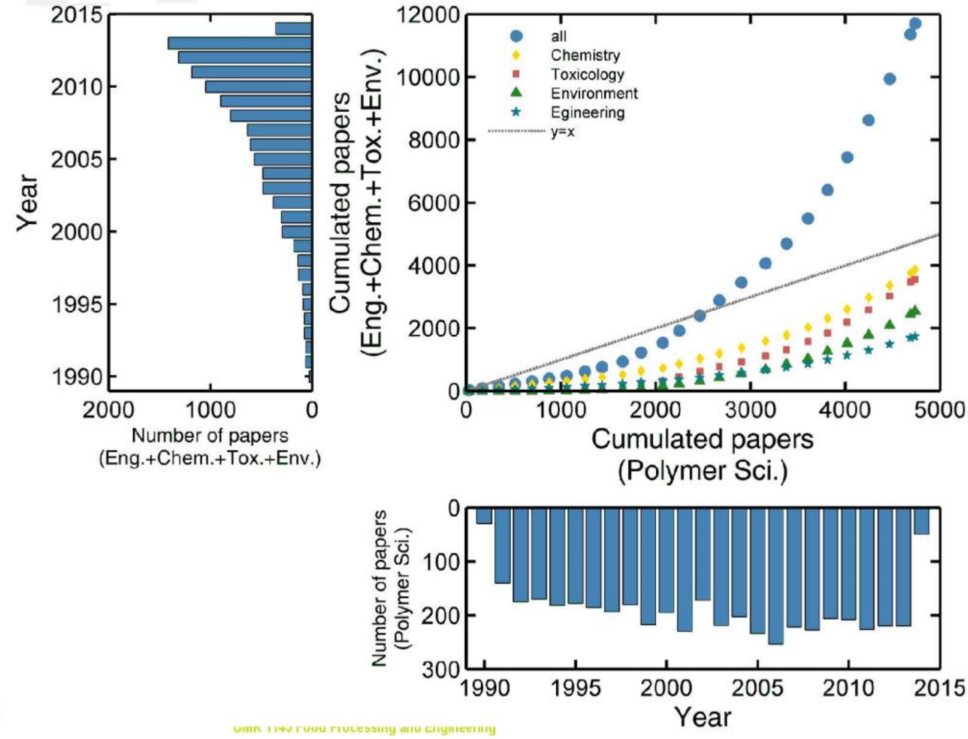
HOW TO REDUCE THE RISK OF CONTAMINATION

Ignorance
Miss-conception

Education
Training
Research

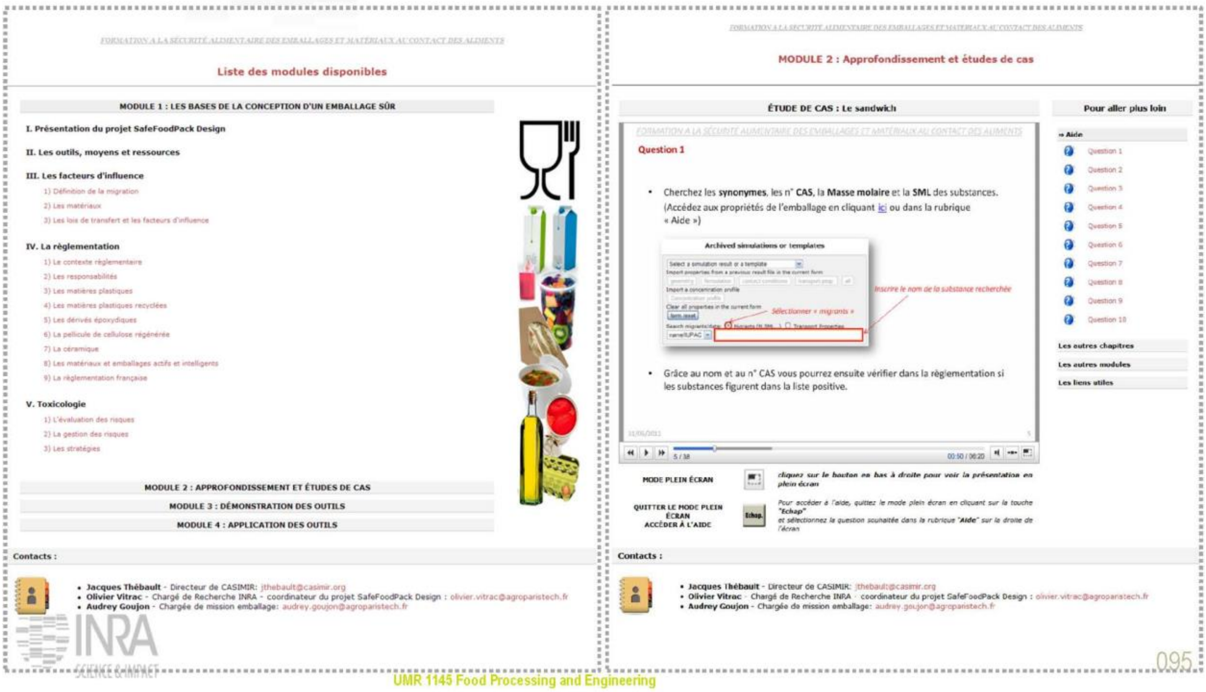
DEVELOPING THE COOPERATION BETWEEN STAKEHOLDERS

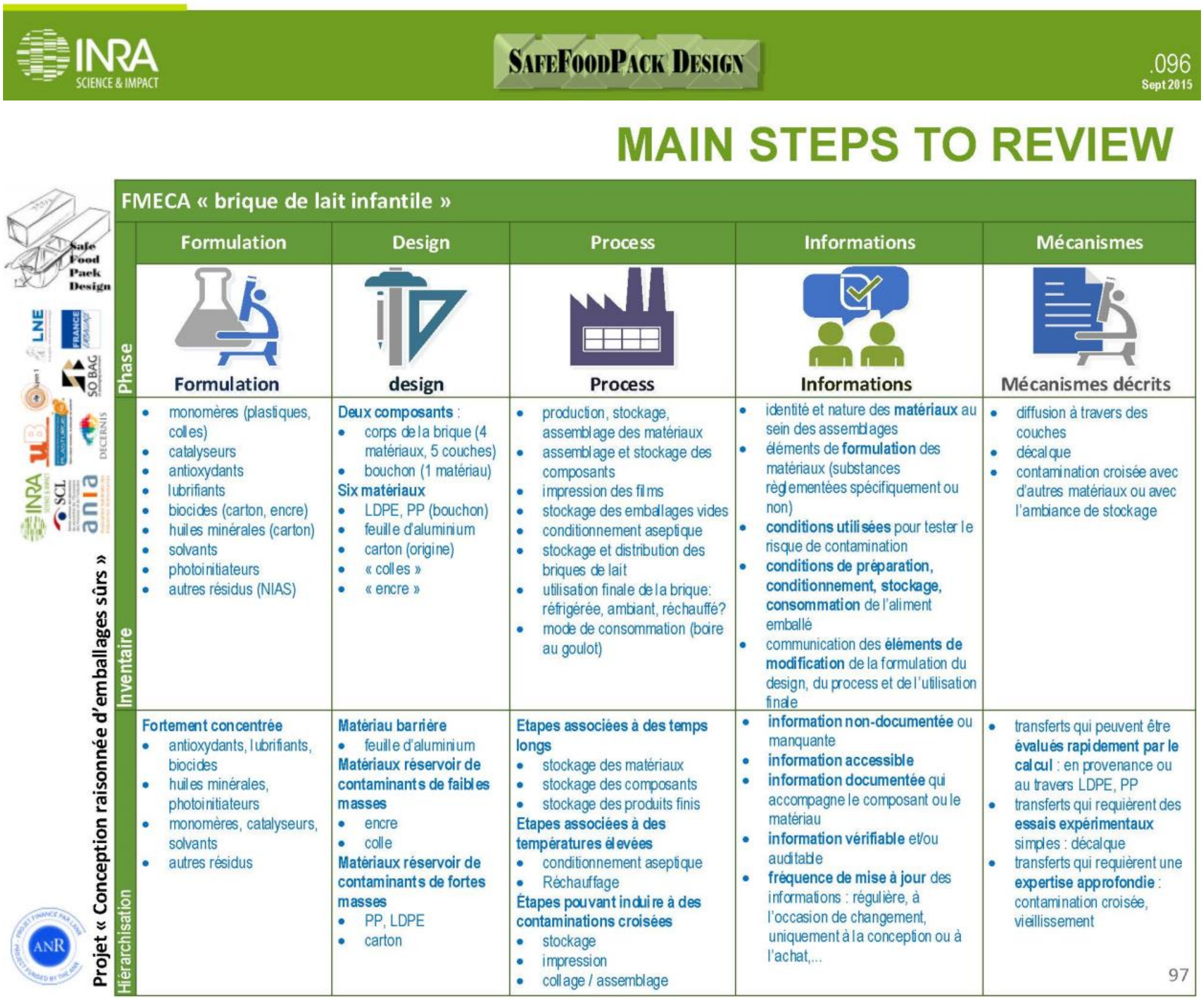


WEBINARS/ONLINE TRAINING

http://modmol.agroparistech.fr/SFPD/training/

http://rmt-propackfood.actia-asso.eu/





FMECA « brique de lait infantile »

	Formulation	Design	Process	Informations	Mécanismes
Phase	Formulation	design	Process	Informations	Mécanismes décrits
Inventaire	• monomères (plastiques, colles) • catalyseurs • antioxydants • lubrifiants • biocides (carton, encre) • huiles minérales (carton) • solvants • photoinitiateurs • autres résidus (NIAS)	**Deux composants** : • corps de la brique (4 matériaux, 5 couches) • bouchon (1 matériau) **Six matériaux** • LDPE, PP (bouchon) • feuille d'aluminium • carton (origine) • « colles » • « encre »	• production, stockage, assemblage des matériaux • assemblage et stockage des composants • impression des films • stockage des emballages vides • conditionnement aseptique • stockage et distribution des briques de lait • utilisation finale de la brique: réfrigérée, ambiant, réchauffé? • mode de consommation (boire au goulot)	• identité et nature des **matériaux** au sein des assemblages • éléments de **formulation** des matériaux (substances réglementées spécifiquement ou non) • **conditions utilisées** pour tester le risque de contamination • **conditions de préparation, conditionnement, stockage, consommation** de l'aliment emballé • communication des **éléments de modification** de la formulation du design, du process et de l'utilisation finale	• diffusion à travers des couches • décalque • contamination croisée avec d'autres matériaux ou avec l'ambiance de stockage
Hiérarchisation	**Fortement concentrée** • antioxydants, lubrifiants, biocides • huiles minérales, photoinitiateurs • monomères, catalyseurs, solvants • autres résidus	**Matériau barrière** • feuille d'aluminium **Matériaux réservoir de contaminants de faibles masses** • encre • colle **Matériaux réservoir de contaminants de fortes masses** • PP, LDPE • carton	**Etapes associées à des temps longs** • stockage des matériaux • stockage des composants • stockage des produits finis **Etapes associées à des températures élevées** • conditionnement aseptique • Réchauffage **Etapes pouvant induire à des contaminations croisées** • stockage • impression • collage / assemblage	• **information non-documentée** ou manquante • **information accessible** • **information documentée** qui accompagne le composant ou le matériau • **information vérifiable** et/ou auditable • **fréquence de mise à jour** des informations : régulière, à l'occasion de changement, uniquement à la conception ou à l'achat,...	• transferts qui peuvent être **évalués rapidement par le calcul** : en provenance ou au travers LDPE, PP • transferts qui requièrent des **essais expérimentaux** simples : décalque • transferts qui requièrent une **expertise approfondie** : contamination croisée, vieillissement

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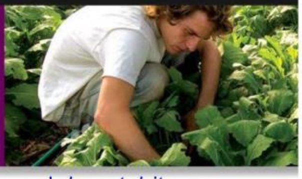


Dr. Olivier Vitrac lectures and workshops

Date: July 1, 2015
Location: School of Packaging, MSU

LECTURES ABOUT

"PREDICTION OF MASS TRANSFER IN POLYMERS"

by OLIVIER VITRAC, Ph.D.

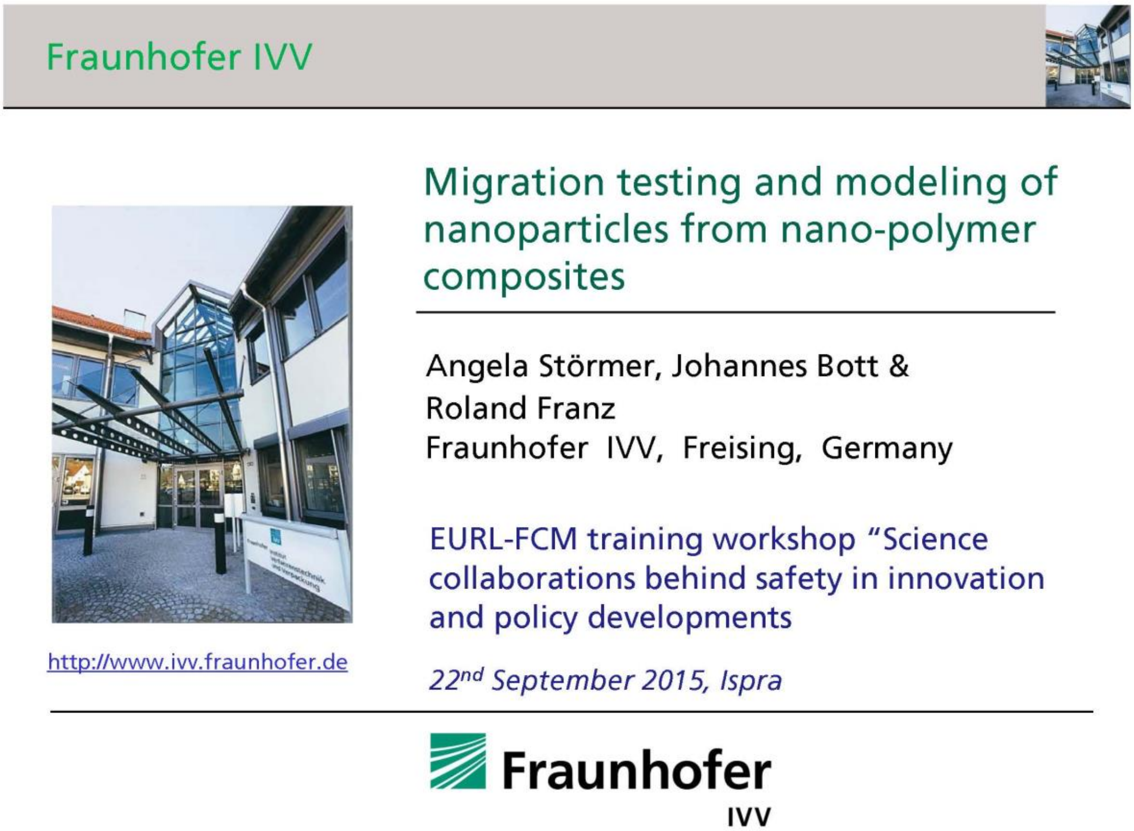
INRA, FRANCE

http://www.canr.msu.edu/events/vitrac
http://www.packaging.msu.edu/industry_testing_services/downloadable_presentations

When	Presentation	Where
29th June (Monday) *10:00am-11:00am*	**Diffusion coefficients of organic solutes in polymers: new perspectives of prediction**	*Conference Center, Room 100, School of Packaging*
30th June (Tuesday) 2:00pm-3:00pm	**An atomistic Flory-Huggins formulation for the tailored prediction of activity and partition coefficients**	*The Ternes Outreach Center, Room 120, School of Packaging* *Registration required*
1st July (Wednesday) 2:00pm-4:00pm	**Workshop: Prediction of the migration: beyond conventional estimates***	*The Ternes Outreach Center, Room 120, School of Packaging* *Registration required*

UMR 1145 Food Processing and Engineering

Migration testing and modeling of nanoparticles from nano-polymer-composites. A collaboration with Plastic Europe, the European Carbon Black Association and from the European Silica producer association - Dr. Angela Stoermer, IVV Fraunhofer institute



Migration potential of NPs in food contact plastics

Agenda

- Overview and summary of experimental model studies on the migration potential of ‚nano additives' from food contact plastics
- Migration modeling for nanoparticles from plastics – some calculations and visualisations of their migratability
- A view into an EFSA Opinion
- Conclusions

Fraunhofer IVV

Migration potential of NPs in food contact plastics

Overview experimental model studies

We did a series of experimental studies (migration tests and other) using LDPE polymer (high diffusion properties, worst case matrix) containing 'nano additives' at various concentrations:

- **Nano-sized titanium nitride, TiN**
  (listed in PIM – 20 ppm in PET)
- **Nano silver**
  (has been used in numerous studies)
- **Carbon black**
  (listed in PIM – 2.5% in polymer)
- **Synthetic amorphous silica (hydrophilic and silanated)**
  (listed in PIM – no restriction)
- **Laponite**
  (a very small nanoclay, still in hands, finished shortly)

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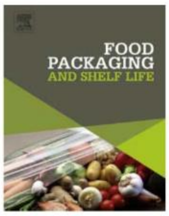
Model system:

Nano titanium nitride (TiN) in LDPE

Bott J, Störmer A and Franz R., A model study into the migration potential of nanoparticles from plastics nanocomposites for food contact. Food Packaging and Shelf Life 2(2) 73-80 (2014). DOI: 10.1016/j.fpsl.2014.08.001.



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IVV

Migration potential of NPs in food contact plastics

Titanium nitride (TiN) in PET bottles for water and soft drinks – a very consumer relevant example

Technical function:

'Reheat additive' -
improves the thermal properties,
increase of production lots

Preforms for PET bottles

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IVV

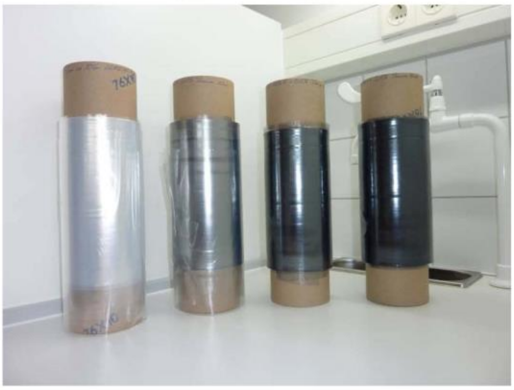
Migration potential of NPs in food contact plastics

Model system: nano TiN in LDPE

Inhouse production of 3 different LDPE films (d = 60 µm) with TiN levels of .....

....0 ppm (blank), 100 ppm, 500 ppm, 1000 ppm

...using a masterbatch of nano TiN (20 nm) in LDPE



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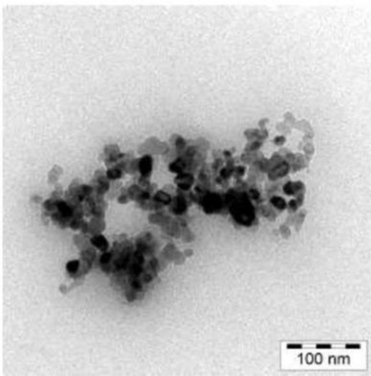
Migration potential of NPs in food contact plastics

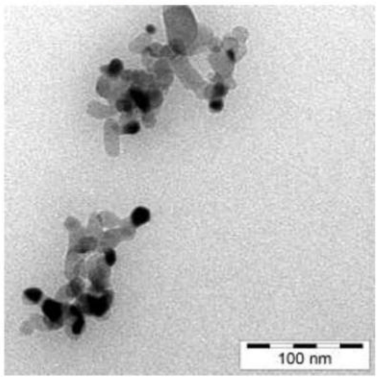
Model system: nano TiN in LDPE

TEM images of the LDPE film with nano TiN at levels of

100 ppm in LDPE



1000 ppm in LDPE



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Migration potential of NPs in food contact plastics

Model system: nano TiN in LDPE

Results migration test 10 d @ 60°C (Ti determined by ICP-MS)

Test film (LDPE)	Food simulant	Ti migration [µg/dm²]	Ti migration [µg/kg]
100, 500, 1000 ppm	3% acetic acid	n.d. $\leq$ 0.040	$\leq$ 0.24
100, 500, 1000 ppm	iso-octane	n.d. $\leq$ 0.017	$\leq$ 0.11
100, 500, 1000 ppm	95% ethanol	n.d. $\leq$ 0.018	$\leq$ 0.11
100, 500, 1000 ppm	0.2 % Novachem	n.d. $\leq$ 0.016	$\leq$ 0.09

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Migration potential of NPs in food contact plastics

Model system:

Nano silver in LDPE

Bott J, Störmer A, and Franz R, 2014. A comprehensive study into the migration potential of nano silver particles from food contact polyolefins. In: Chemistry of Food and Food Contact Materials: From production to plate. Benvenuto M A, Ahuja S, Duncan T V, Noonan G, Roberts-Kirchhoff E. Eds: ACS Symposium Series 1159, American Chemical Society, Washington DC, US. doi:10.1021/bk-2014-1159.ch005.

Fraunhofer IVV

Migration potential of NPs in food contact plastics

Model system: nano silver in LDPE

Inhouse production of 3 different LDPE films (100 µm) with nano silver at levels of .....

....0 ppm (blank), 50 ppm, 185 ppm and 250 ppm

...using a commercial masterbatch of nano Ag in LDPE

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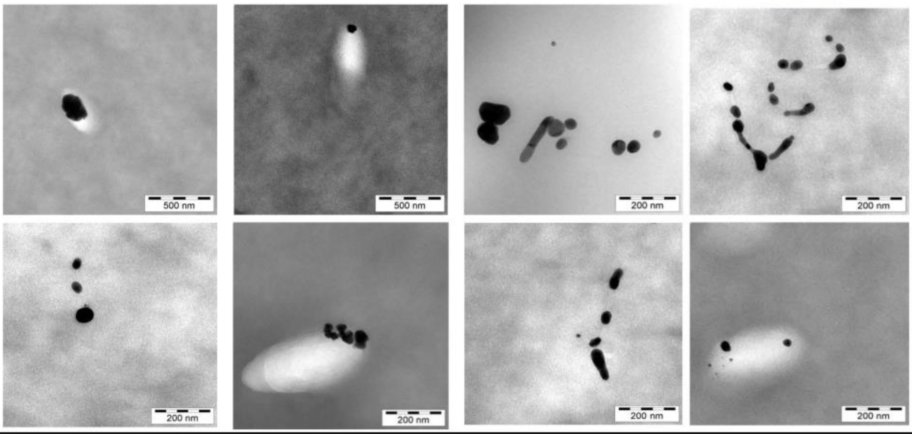
Migration potential of NPs in food contact plastics

Model system: nano silver in LDPE

TEM images of the worst-case test material:
LDPE film (100 µm) with nano-silver at 250 ppm



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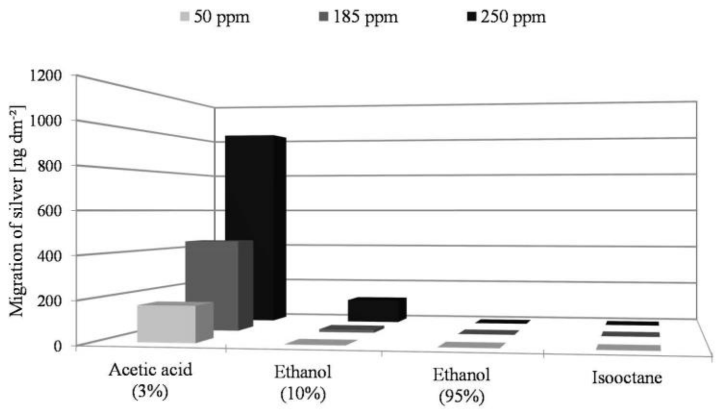
Migration potential of NPs in food contact plastics

Model system: nano silver in LDPE

Silver migration from nano Ag LDPE films after 10 days @ 60°C

Comparison:
3% acetic acid versus all other simulants (total silver measured by ICP-MS)



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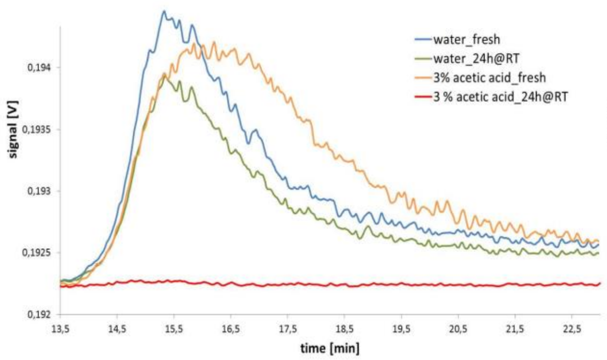
Migration potential of NPs in food contact plastics

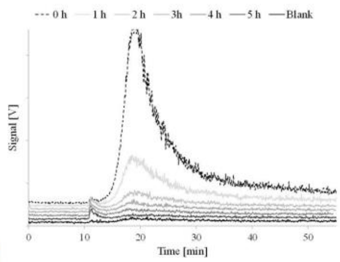
Model system: nano silver in LDPE

Question: Is Ag as determined by ICP-MS nano Silver?

Test: AF4 analysis 1 ppm nano silver: silver rapidly dissolves to ions



Ag nanoparticles in 3 % acetic acid (orange, red) and water (blue, green) at RT.
In water 80 % of initial particles still present after 24 h.



Ag nanoparticles in 3 % acetic acid at RT:
Half life of particles: 0.6 h

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Migration potential of NPs in food contact plastics

Model system:

Carbon Black in LDPE and PS

Bott J., Stoermer A. and Franz R.: Investigation into the migration of nanoparticles from plastic packaging materials containing carbon black into foodstuffs. Food Additiv. Contam. Vol. 31 (10), 1769–1782 (2014). DOI: 10.1080/19440049.2014.952786.

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Migration potential of NPs in food contact plastics

Summary of all studies experimental results:

In ALL cases, migration studies even when using exaggerated contact conditions of food simulants with the test films, no analytical (ICP-MS, AF4) observation of migrated nanoparticles was obtained.

The achieved detection limits were dependent on the type of nano additive and ranged from 0.02 µg/dm² - 0.5 µg/dm² (0.12 µg/kg - 0.5 µg/kg food) and were in two other cases at 5 ppb and 130 ppb.

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Migration modeling of nano particles from food contact plastics

Intention:

…. to support and substantiate our experimental results and other findings

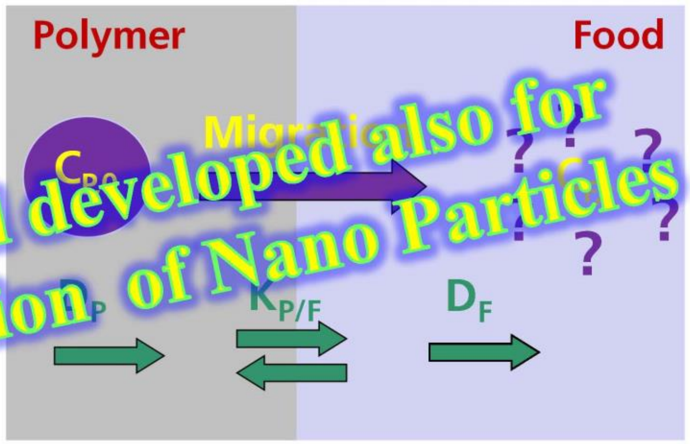
…. to explore into the concentration range not accessible to analytical determinations

Migration modeling of nanoparticles

'Conventional' migration from FCM plastics can be modeled today …

…when mass transport follows Fickian Law

$$\frac{\partial c}{\partial t} = D \frac{\partial^2 c}{\partial x^2}$$



Model developed also for migration of Nano Particles

Key-Parameter: Diffusion coefficient D_P & partition constant $K_{P/F}$

Migration potential of NPs in food contact plastics

Migration modeling of NPs for PET

Journal of Applied Polymer Science

A New Method for the Prediction of Diffusion Coefficients in Poly(ethylene terephthalate)

Frank Welle
Fraunhofer Institute for Process Engineering and Packaging IVV, Giggenhauser Straße 35, Freising 85354, Germany
Correspondence to: F. Welle (E-mail: welle@ivv.fraunhofer.de)

$$D_P = b\left(\frac{V}{c}\right)^{\frac{a-\frac{1}{T}}{d}}$$

Parameter	Value
a	$1.93\ 10^{-3}\ K^{-1}$
b	$2.37\ 10^{-6}\ cm^2\ s^{-1}$
c	$11.1\ Å^3$
d	$1.50\ 10^{-4}\ K^{-1}$

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Migration potential of NPs in food contact plastics

Migration modelling of nanoparticles - PET

D_P = f (molecular volume)

Journal of Applied Polymer Science
A New Method for the Prediction of Diffusion Coefficients in Poly(ethylene terephthalate)
Frank Welle
Fraunhofer Institute for Process Engineering and Packaging IVV, Giggenhauser Straße 35, Freising 85354, Germany
Correspondence to: F. Welle E-mail: welle@ivv.fraunhofer.de

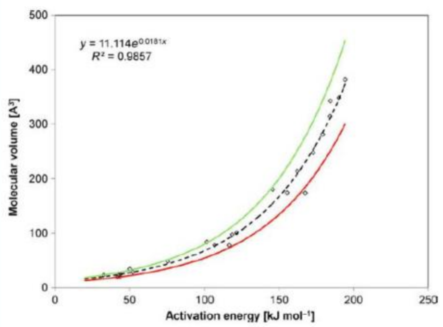

Figure 3. Correlation of the experimentally determined activation energy of diffusion E_A with the calculated volume of the migrants, red and green lines: variance of 20% on the molecular volume V. [Color figure can be

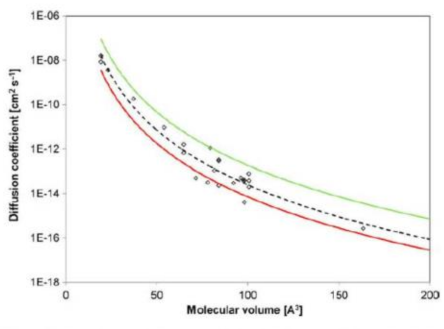

Figure 5. Correlation of literature of the diffusion coefficients in PET at 35°C and 40°C (Table 3 in Ref. 18) with the calculated molecular volume, black line: predicted diffusion coefficients from eq. (9), green and red line: variance of ±20% of the molecular volume V. [Color figure can be

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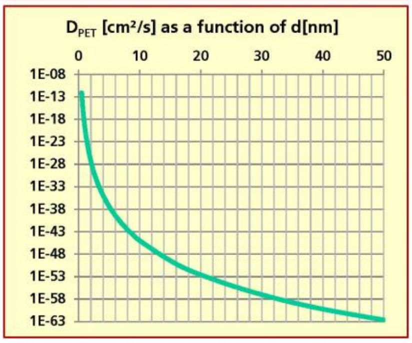
Migration potential of NPs in food contact plastics

Migration modeling for PET - diffusion coefficients at 40°C

Activation energy increases dramatically with d !
Diffusion coefficients become absurdly low!
=> No Migration



d [nm]	V [nm³]	E_a [kJ/mol]	D_{PET} [cm²/s]
0,5	0,1	98,3	7,726E-13
1	0,5	213,6	1,9026E-20
2	4,2	328,8	4,737E-28
3	14,1	396,3	1,6834E-32
4	33,5	444,1	1,1731E-35
5	65,4	481,2	4,1752E-38
6	113,1	511,5	4,1686E-40
7	179,6	537,1	8,4808E-42
8	268,1	559,4	2,905E-43
9	381,7	578,9	1,4814E-44
10	523,6	596,5	1,034E-45
15	1767,1	663,9	3,6743E-50
20	4188,8	711,7	2,5605E-53
30	14137,2	779,1	9,099E-58
40	33510,3	827,0	6,3408E-61
50	65449,8	864,1	2,2568E-63

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Migration potential of NPs in food contact plastics

Model study & migration modeling of nanoparticles

FOOD PACKAGING AND SHELF LIFE 2 (2014) 73–80

Available online at www.science[...]
ScienceDirect
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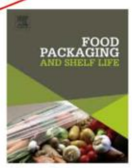

A model study into the migration potential of nanoparticles from plastics nanocomposites for food contact

CrossMark

J. Bott, A. Störmer, R. Franz*

Fraunhofer Institute for Process Engineering and Packaging IVV, Giggenhauser Straße 35, 85354 Freising, Germany

Fraunhofer IVV

Migration potential of NPs in food contact plastics

Migration modelling of nanoparticles - Polyolefines

For PO's a correlation between molecular volume and activation energy respectively diffusion coefficient as established for PET is not available.

⇒ Need of a different approach

<u>IDEA</u>:

- Surrogate Nanoparticles with worst case character: spheres consisting or a material with low molecular weight (m.w.) and assuming a low density
- Calculate m.w. as a function of diameter
- Calculate D_P as function of m.w. using the PIRINGER's equation (socalled 'exact equation')

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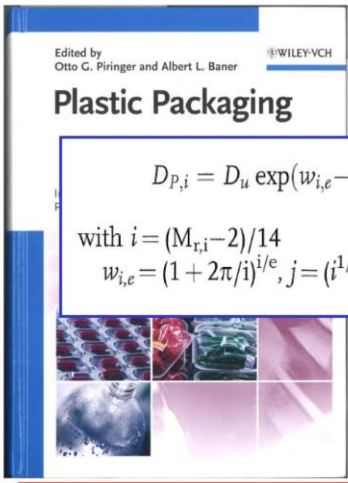
Migration potential of NPs in food contact plastics

Migration modelling of nanoparticles - polyolefines



$$D_{P,i} = D_u \exp(w_{i,e} - w_{p,e} \cdot 0.14(14j+2)^{2/3} - ww_{j,e}^{2/3} T_{m,p} R/RT) \qquad (6.28)$$

with $i = (M_{r,i} - 2)/14$

$w_{i,e} = (1 + 2\pi/i)^{i/e}$, $j = (i^{1/3})$, $w_{j,e} = (1 + 2\pi/j)^{j/e}$, $p = (M_{r,p}/14)^{1/3}$, $w_{p,e} = (1 + 2\pi/p)^{p/e}$

PIRINGER equation (6.28): so-called ,'exact' equation for Polyethylene < T_{mp}

$$D_{P,i} = f(T,\ m.w._{Migrant},\ m.w._{Polymer},\ T(m.p.)_{Polymer})$$

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Migration potential of NPs in food contact plastics

Migration modeling of nano particles:

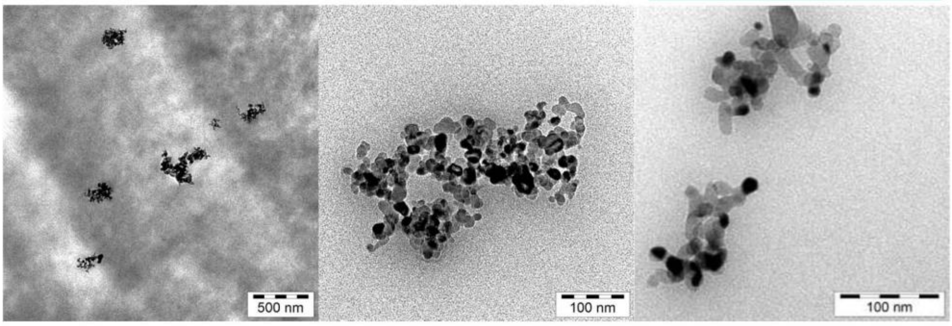
Example: 1000 ppm of NP (TiN) in LDPE (d = 3 mm)

Contact: 10 days @ 40°C


ScienceDirect

A model study into the migration potential of nanoparticles from plastics nanocomposites for food contact

J. Bott, A. Störmer, R. Franz



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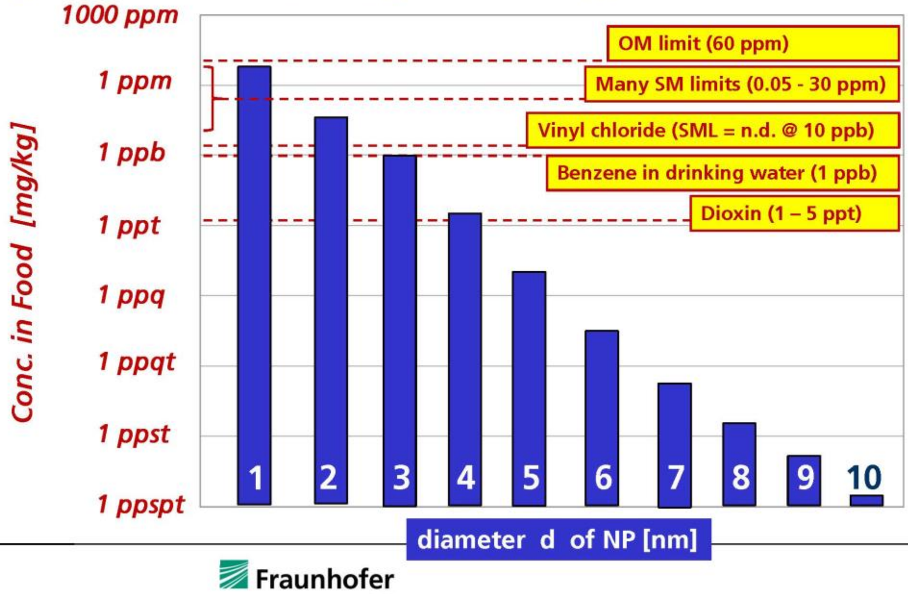
Can nano particles migrate from FC plastics into foods?

Migration (10d@40°C) modeling of NPs (1000 ppm in LDPE)



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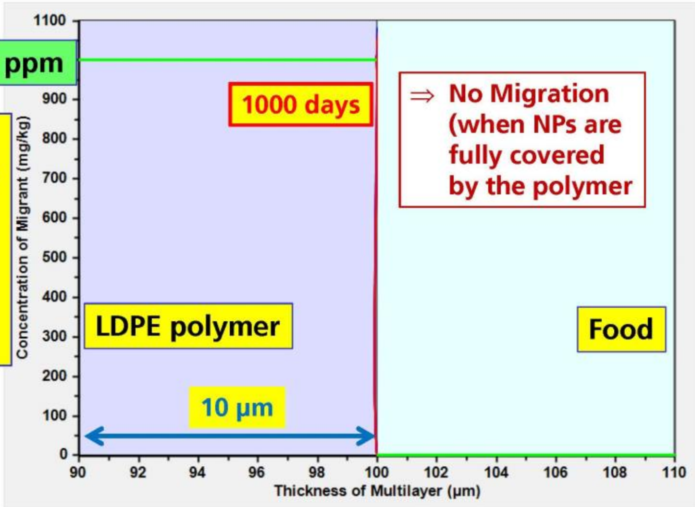
Can nano particles migrate from FC plastics into foods?

Migration modelling - concentration profile: LDPE

LDPE of 100 µm thickness with a nano additive of 5 nm (diam.)

T = 40°C
t = 1000 days



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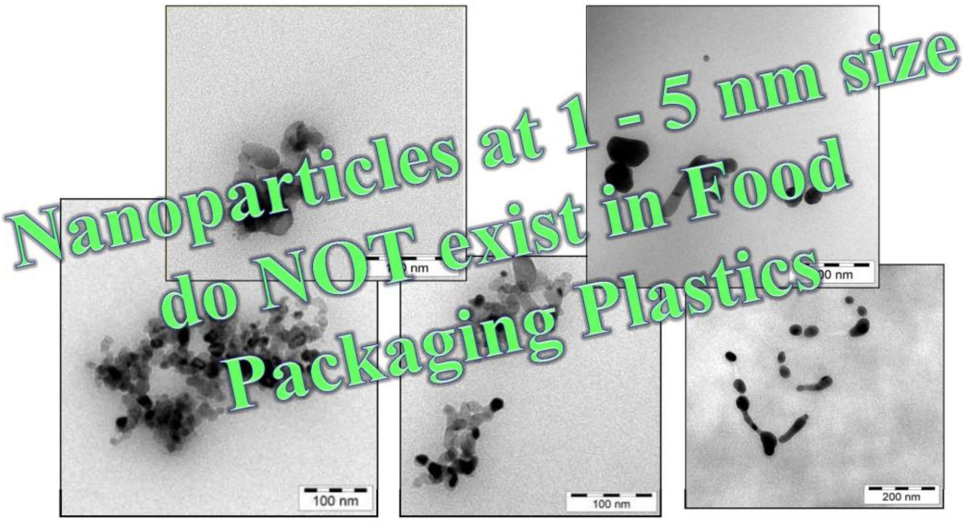
Can nano particles migrate from FC plastics into foods?



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Migration potential of NPs in food contact plastics

EFSA opinion on an additive (impact modifier in PVC) in nanoform

efsa
European Food Safety Authority

EFSA Journal 2014;12(4):3635

SCIENTIFIC OPINION

Scientific Opinion on the safety assessment of the substances (butadiene, ethyl acrylate, methyl methacrylate, styrene) copolymer either not crosslinked or crosslinked with divinylbenzene or 1,3-butanediol dimethacrylate, in nanoform, for use in food contact materials[1]

EFSA Panel on Food Contact Materials, Enzymes, Flavourings and Processing Aids (CEF)[2, 3]

European Food Safety Authority (EFSA), Parma, Italy

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Migration potential of NPs in food contact plastics

EFSA opinion on an additive (impact modifier in PVC) in nanoform

"Recognized migration modelling, as currently settled, is not directly applicable to nanoparticle migration estimation. For this reason, the applicant applied additional conservative assumptions to estimate migration of the nanoparticles from the nanocomposite material, in particular the assumption that all particles had a size less than 10 nm. The estimated migration was 1 x10^{-6} mg/kg food. **Real migration, if any, is expected to be even lower and therefore consumer exposure would be very low, if any** (Bott et al., 2014).
Consequently, **the Panel considered that the intended use of these nanoparticulate substances does not give rise to exposure of the consumer via food** and therefore would not be of toxicological concern if used only in rigid PVC individually or in combination up to a total of 10 % w/w and for the food contact applications described."

Bott J, Störmer A, and Franz R, 2014. A comprehensive study into the migration potential of nano silver particles from food contact polyolefins. In: Chemistry of Food and Food Contact Materials: From production to plate. Benvenuto M A, Ahuja S, Duncan T V, Noonan G, Roberts-Kirchhoff E. Eds: ACS Symposium Series 1159, American Chemical Society, Washington DC, US. doi:10.1021/bk-2014-1159.ch005.

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Migration potential of NPs in food contact plastics

Conclusions

- Our migration studies did not show any evidence that NPs would migrate from the LDPE host polymer into food simulants even under very severe test conditions.

- Migration modeling indicates that NP larger than 3 - 4 nm in diameter cannot migrate (following Fick'ian law of diffusion) at all from LDPE and therefore not from any plastics FCM. For PET, the cut-off value would be below 1 nm. However, usual primary NPs are already larger. And, due to aggregation and agglomeration of NP such small single NP do not occur in FCM.

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Migration potential of NPs in food contact plastics

Conclusions

- Experimental results and theoretical considerations (migration modeling) strongly underpin the assumption that NPs are immobilised when fully incorporated in FCM plastics (no direct contact).

  From this exposure of the consumer via ingestion can be excluded.

- Whether mechanical stress or strong interactions with foods (swelling) of the polymer surface may cause physical release should be considered in the particular case and be checked.

Fraunhofer IVV

Thank you!

This work was supported by

- PlasticsEurope
- the Bavarian State Ministry of Environment and Public Health within the project 'LENA' on Nanotechnology related Food Safety coordinated by the Bavarian Authority for Public Health and Food Safety (LGL)
- International Carbon Black Association ICBA
- Association of Synthetic Amorphous Silica Producers ASASP

which is greatly acknowledged!

Many thanks also to Johannes Bott, our Ph.D. student who has done the experimental work including test sample preparations.

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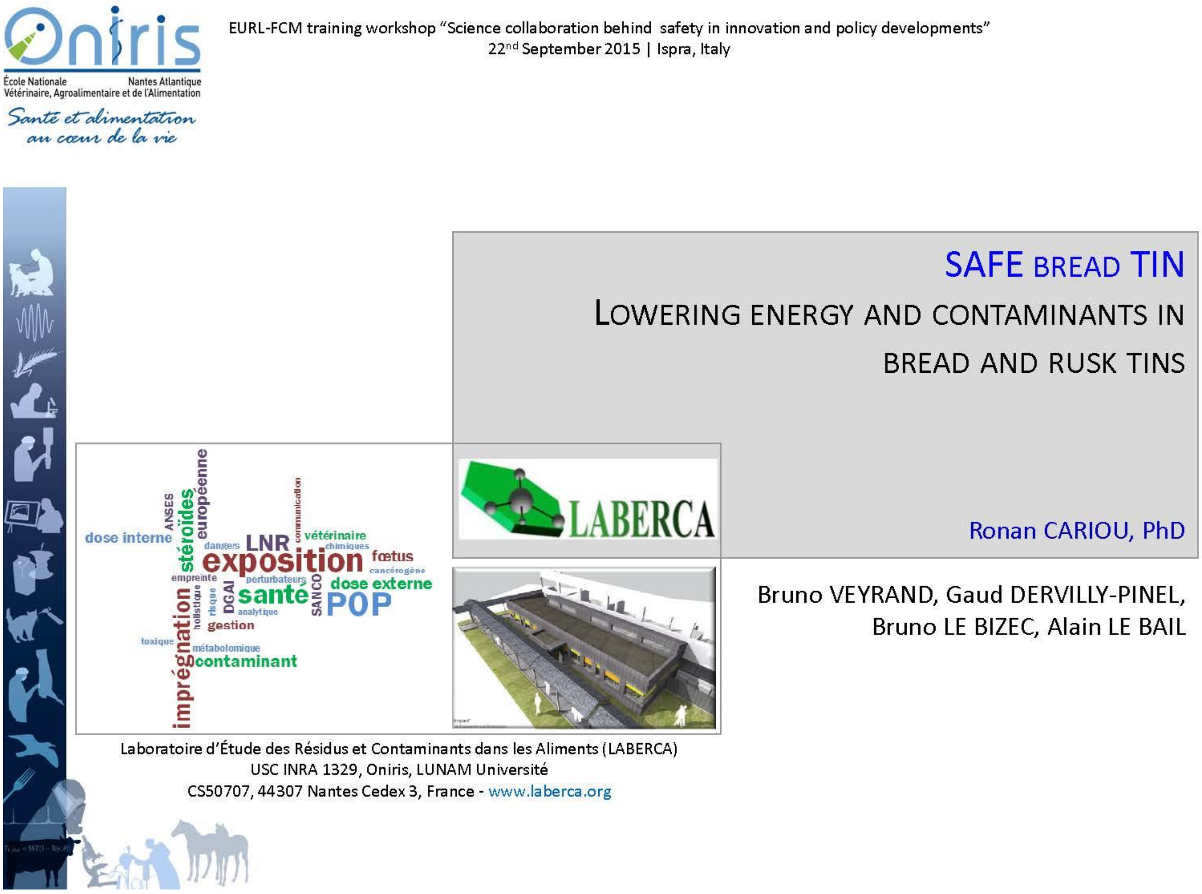
SAFE bread TIN: lowering energy and contaminants in bread and rusk tins - Dr. Ronan Cariou, ONIRIS



Outline

1. Oniris

2. SAFE bread TIN project

3. LABERCA

Oniris

Nantes Atlantic College of Veterinary Medicine, Food Science and Engineering

- Merging of Veterinarian and Agriculture Engineer schools

Oniris

Nantes-Atlantic National College of Veterinary Medicine, Food Science and Engineering

http://www.oniris-nantes.fr/en/

LABERCA

http://www.laberca.org/

GEPEA

http://www.gepea.fr/

- Process Engineering for Environment and Food
- Joint Research Unit between Oniris and École des Mines of Nantes (UMR CNRS 6144)

SAFE bread TIN project — Consortium

Lowering energy and contaminants in bread and rusk tins

PROJET FINANCÉ PAR L'ANR – PROJECT FUNDED BY THE ANR ~1 060 000 €

2012–2016

AGENCE NATIONALE DE LA RECHERCHE

Sustainable food systems call

GEPEA

Cemagref — Baking modelling

Coord.: Pf Alain LE BAIL — Baking modelling

Steering committee
C. Simoneau

Maé — SME
Industrial coating

Industrial bread manufacturer

LABERCA — Chemical analyses (migrants)

AgroParisTech — Rheology, Chemical analyses (Maillard)

LPIM Mulhouse — Polymer science

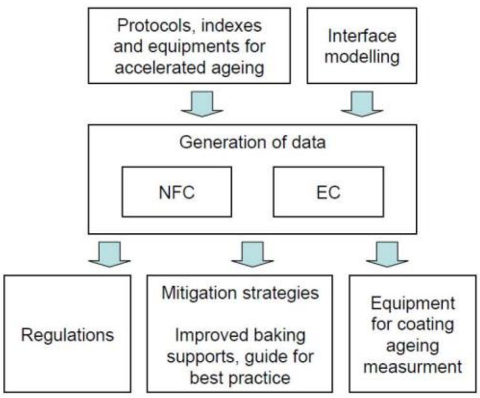
Holo3 — Technology transfer center, Optical technologies

SAFE bread TIN project — Objectives

Lowering energy and contaminants in bread and rusk tins

=> Ageing of anti stick coating

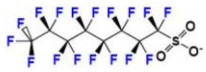
- Bread depanning / stickiness
- Chemical risk (neoformed, exogenous)
- Non destructive sensors: detection of end of life
- Innovative pan coating and process



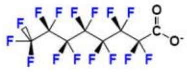
SAFE bread TIN project — Task 1

Establishment of the material and methods

- Reference baking test (recipe, geometry, *etc.*) — Industrial bread manufacturer
- Pan index based on protocols for coating properties (tribology tests / surface scrapping, wettability, hardness, roughness, surface morphology, spectroscopy)
- Analysis of PFAS migrants



PFOS

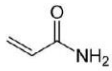


PFOA

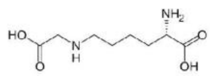
- Analysis of neoformed

Hydroxymethylfurfural

Furan



Acrylamide

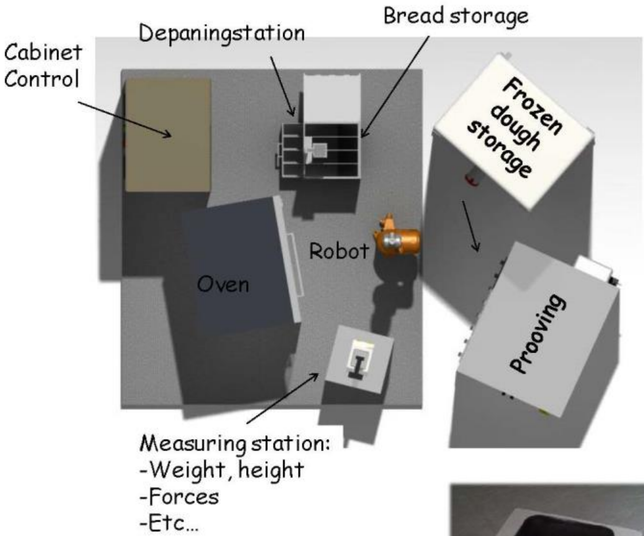


Carboxymethyllysine

SAFE bread TIN project — Task 1

- Automatic baking machine at pilot scale – accelerated ageing of pans

GEPEA



Miniaturized pans

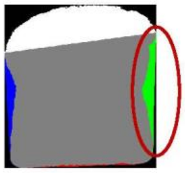
SAFE bread TIN project — Task 2

Baking process

- Heat transfer models needed to predict

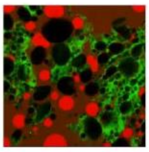
  Crust formation as fct of time-temperature

  Relationship between coating structure and baking



- Baking studies

  Bread properties



- Partial vacuum baking

  Lower temperature

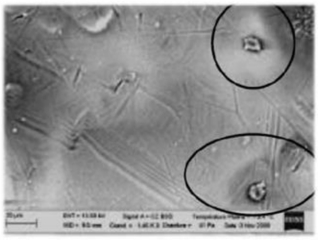
  ↘ Energy ↘ Migration ↘ Maillard

SAFE bread TIN project — Task 3

Crust pan interface

- Characterisation of coating ageing

  Tribology, imaging, functionality



- Chemistry of the crust

- Prototype pans

SAFE bread TIN project — Tasks 4 & 5

Task 4: accelerated ageing at pilot scale (2000 cycles)

- Kinetic study (every 200 cycles)

  Analysis of PFAS — LABERCA

  Analysis of neoformed compounds — AgroParisTech, InVivo Labs

  Analysis of coating (multispetral) — LPIM Mulhouse, Holo3

  Crust evolution — Spectralys innovation

Task 5: accelerated ageing at industrial scale (12 months)

Similar to Task 4, adjustments — Industrial bread manufacturer

SAFE bread TIN project — Tasks 6 & 7

Task 6: Finalized solutions

- Coating and operation guide — Maé
- Equipment for ageing evaluation — Holo3
- Equipment for crust assessment — AgroParisTech
- Guide for good practices for FCM undergoing thermal cycling

Task 7: Dissemination

- Various targets (industry, authorities, academic)

FINAL CONFERENCE – SATIN PROJECT

NON STICK COATING IN THE BAKING INDUSTRY
TECHNOLOGICAL, CHEMICAL and REGULATORY ISSUES

PARIS - 28-29 JUIN 2016

http://satin-baking.fr/

SAFE bread TIN project — Other considerations

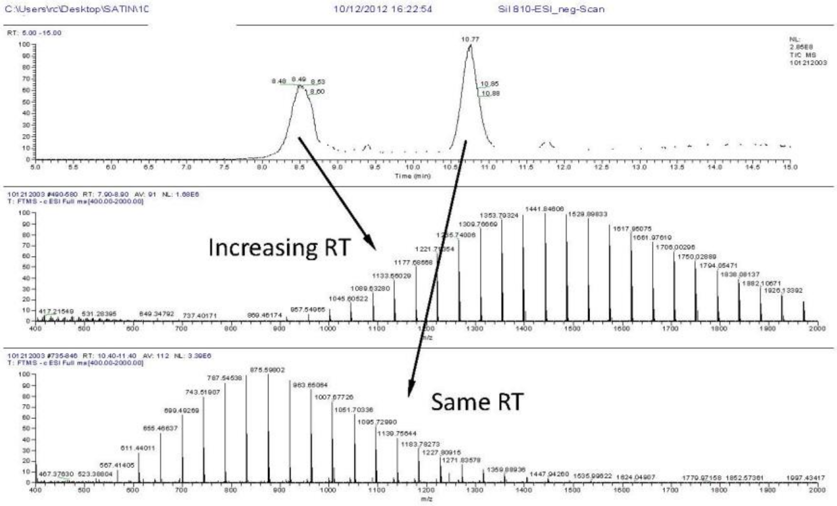
Disclaimer

Pf Alain LE BAIL

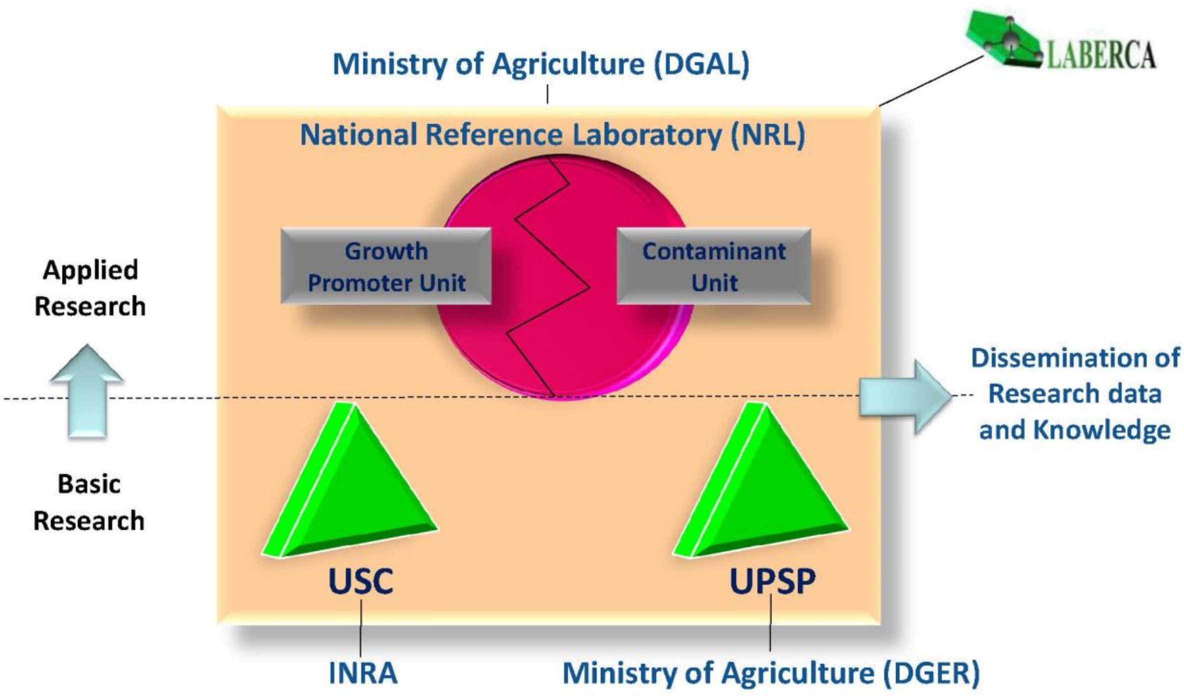
alain.lebail@oniris-nantes.fr

Chemical nature of coating

- Resin by LC-HRMS
- Ethoxylate pattern



LABERCA — ~50 collaborators



LABERCA — Analytical facilities

UPLC-MS/MS (x 1)

HPLC (x 2)

GC-MS (x 3)

LC-HRMS^n (x 3)

GC-MS/MS (x 2)

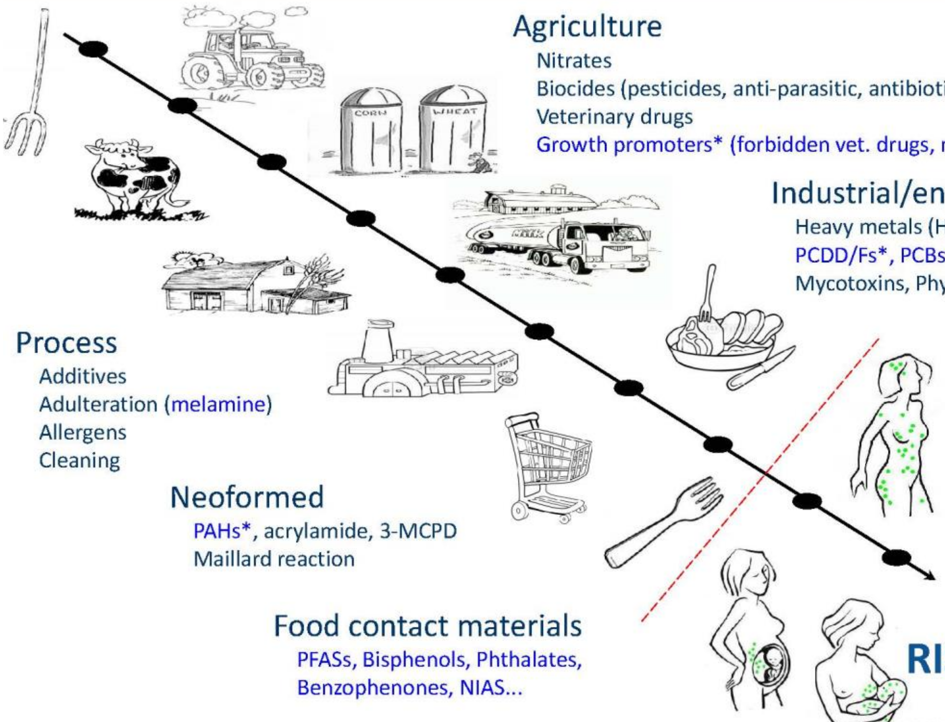
LC-MS/MS (x 2)

UPLC-IM-HRMS (x 1)

GC-HRMS (x 3)

GC-C-IRMS (x 3)

LABERCA — From farm to fork, and beyond



Agriculture
- Nitrates
- Biocides (pesticides, anti-parasitic, antibiotics)
- Veterinary drugs
- Growth promoters* (forbidden vet. drugs, natural hormones)

Industrial/environmental
- Heavy metals (Hg, Pb, Cd, Zn)
- PCDD/Fs*, PCBs*, BFRs, PFASs
- Mycotoxins, Phycotoxins

Process
- Additives
- Adulteration (melamine)
- Allergens
- Cleaning

Neoformed
- PAHs*, acrylamide, 3-MCPD
- Maillard reaction

Food contact materials
- PFASs, Bisphenols, Phthalates,
- Benzophenones, NIAS...

RISK ANALYSIS

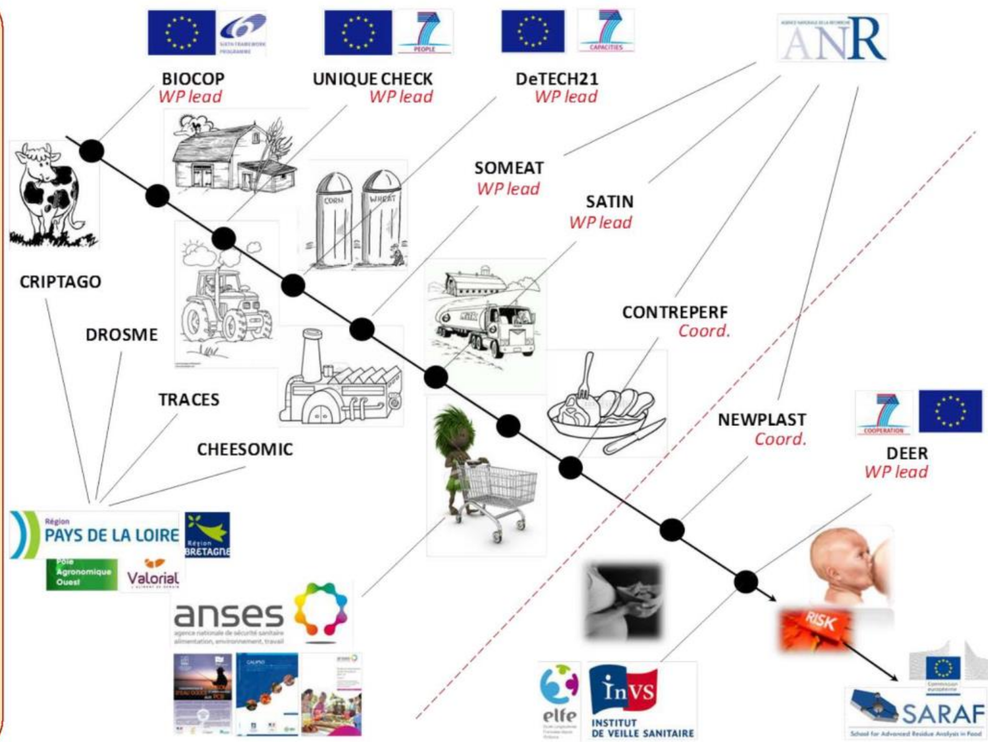
FEED & FOOD

HUMAN FLUIDS & TISSUES

*National Reference Laboratory (NRL)

LABERCA

- Uninterrupted participation to EU projects (FP4 → FP7, …H2020)
- National Research projects (ANR, ANSES, ANSM, PNRPE…)
- Support for public policies (ANSES, InVS…)
- Regional support for agribusiness sector



Acknowledgements

Financial support

The French National Research Agency

ANR AGENCE NATIONALE DE LA RECHERCHE

http://www.laberca.org
http://www.saraf-educ.org

LABERCA

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Migration testing guidelines- a professional association initiative for the non harmonised areas - Peter Oldring, Facet Industry group

Why some migration conditions for plastics are not appropriate for other FCMs.

Peter Oldring
Representing numerous associations directly or indirectly involved in FCMs
NRLs 22nd September 2015 JRC

1

Associations & Bodies participating in Initiative

▪ ACE	Beverage cartons
▪ APEAL	Steel for packaging
▪ CEFIC-FCA	Suppliers of food contact additives
▪ CEPE	Can coating manufacturers
▪ CEPI	Paper industry
▪ EAA	Aluminium
▪ EEA	Porcelain enamelled articles
▪ EMPAC	Rigid metal packaging
▪ ETRMA	Rubbers
▪ EuPIA	Printing inks
▪ EWF	Wax federation
▪ FEC	Housewares, all materials, non-stick for this work
▪ FEFCO	Corrugated packaging
▪ FEICA	Adhesives and sealants
▪ FPE	Multi-material flexible packaging
▪ GAE	Glass Alliance Europe
▪ CELIEGE	Cork
▪ CES Silicones Europe	Silicone elastomers
▪ INSTITUTE NEHRING	Test house
▪ JRC – as observers	

2

DISCLAIMER

- I am not an analyst.
- I cannot do analytical chemistry.
- However, I have to understand and work with – make decisions etc., – analytical data, in order to determine the safety of my company's products.
- The work is embryonic and associations are still joining and the final format will certainly be different to that initially envisaged, but as of yet we do not know how different.

3

The Issue - 1

- In the Plastics Regulation (10/2011) and supporting documentation, i.e. Migration Guidelines, some of the simulants, times and temperatures are inappropriate for non-harmonised FCMs (Food Contact Materials).
- However in the absence of harmonised regulations the conditions used in the Plastics Regulation are often applied to non-plastics.
- National Regulations for non-harmonised FCMs are tending to adopt the conditions in 10/2011 – example proposed coating regulations for both Netherlands and Belgium, although different in detail.

4

The Issue - 2

- Obtaining higher levels of migrants under inappropriate conditions may result in mis-interpreting the results, particularly if the simulant, time and temperatures specified in 10/2011 cause deterioration or physico-chemical change of the substrate leading to an overestimation of migration compared to that in foodstuffs.

5

Industry response - 1

- Members of associations have formed a task to offer testing better adapted to the specificity of various materials/ sectors.
- JRC was requested to have an advisory capacity as they were responsible for leading the drafting of the technical guidelines for plastics (reg. 10/2011) and have currently a brief to look at non harmonised FCM
- Each sector is assessing the applicability or not of the plastics 10/2011 migration testing guidelines for their own sector.

6

Industry response - 2

- In some cases they are applicable for other FCM but in some cases they are not
- Gaps or lack of feasibility of implementations are identified and expertise collected and shared to offer technical solutions for improved compliance testing.
- Test proposals are based on technical / scientifically demonstrated justification.
- The Task Force are developing their own compliance guidelines with separate chapters for each non-harmonized FCM:

7

Industry response - 3

- Chapters
  - ➢Introduction
  - ➢FCM specific chapters
    - FPE
    - Adhesives
    - Light metal packaging
    - Paper & Board
    - Silicones
    - Rubbers & TPE
    - Coatings not covered elsewhere
      - – Further sub-divided: work in progress

8

Industry response - 4

- Can – EMPAC / CEPE
- Heatseal – EuPIA / FEICA / FPE
- Coldseal - EuPIA / FEICA / FPE
- Coatings on plastic film CEPE (part)
- Non-stick – FEC / CEPE / CEFIC
- Coatings on Paper and board – CEPI / CITPA
- Heavy duty – CEPE
- Polymeric Coatings on glass – CEPE?
- Coatings on metal foil – FPE / CEPE
- Passivation coatings on metals - APEAL
- SOL-GEL Non-stick coatings – FEC
- Others

9

Industry response - 5

- Each FCM sector applies the common format for Material Specific Guidelines for Conformity Testing
- Scope
  - Uses
- Definitions
- Material Specific Properties to be considered when testing this class of FCM
  - Brief outline as to why plastic testing guidelines may be inappropriate

10

Industry response – 6

- Test Procedures
- Evaluation of test results
- Annexes
  - Annex 1: Reasons why plastic guidelines are not suitable for this class of FCM.
  - Annex 2: References
- The amount of detail in each sector's chapters will very considerably, e.g. silicones are relatively specific to bake ware, whereas adhesives cover the majority of adhesives with different issues for different adhesives.

11

Industry response - 7

- During meetings, different FCM sectors found that other sectors had similar problems with some simulants, times or temperatures.
- There is still debate as to whether to tackle the subject substrate by substrate or material by material e.g. baking paper as paper or as flouro-polymers, silicones etc.
- Some examples of the issues and proposed solutions follow.

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Issues with 3% Acetic Acid for Overall Migration

13

3% Acetic Acid – 1

- A general issue common to many FCM sectors is the use of 3% acetic acid for overall migration (OM).
- OM is NOT a measure of safety, but of inertness.
- Acetic acid corrodes aluminium, either as a coated substrate or foil layer in a multi-layer FCM.

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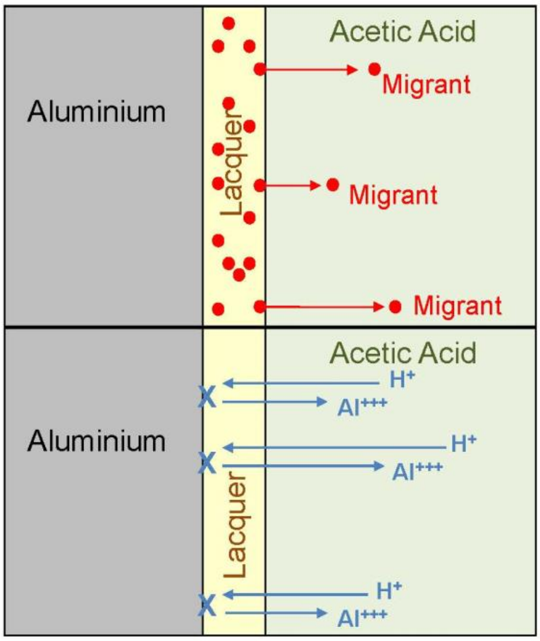
3% Acetic Acid - 2

- Two quite distinct processes are happening during the test
  - True **Migration** – a physical transfer of substances from the **organic** lacquer into the food simulant
  - **Corrosion** – a chemical reaction between acetic acid and the aluminium foil/substrate causing the formation of aluminium acetate and the release of aluminium ions into the food simulant

Schematic Illustration



3% Acetic Acid – 3

- High test results can be obtained, because when the simulant is evaporated to dryness and the residue weighed, the residue is largely aluminium acetate salts
- This increases the weight of the residue, for example:
  - Aluminium molecular weight = 27
  - Aluminium triacetate molecular weight = 204
- Hence up to 87% of the measured result is due to the simulant, not to the aluminium (ions) released.

16

3% Acetic Acid – 4

- For FPE the overall migration from coated aluminium foil is their biggest issue.
- Coatings for rigid metal packaging also have a major issue with 3% acetic acid.
- The use of citric acid has been proposed, but this has the drawback that in practice it is not volatile enough for a gravimetric determination of overall migration by evaporation.

17

3% acetic acid – 5

- Proposals being investigated for FPE and coated rigid metal packaging include:
  - 3% acetic acid being used for the extraction, BUT only the chloroform soluble organic material is weighed.
    - Extract in 3% acetic acid, then mix chloroform with the extract, separate the phases and then evaporate the chloroform soluble part to dryness before weighing. Need to confirm that all of the organic material is extracted.
  - For can coatings the use of stainless steel panels and silver foil is being investigated in order to validate chloroform approach.

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Issues with Olive Oil and Silicone Elastomers

19

Silicone Elastomers - 1

- Silicones are exempted from (EU) N° 10/2011 given that elastomers have different physico-chemical properties compared to plastics
- Problems for silicone elastomers arise mainly with compliance testing for baking moulds

Silicone Elastomers - 2

- Olive / vegetable oils contain components penetrating into the silicone elastomer matrix, which results in an overestimation of migration compared to real food. The same applies to its substitutes iso-octane and 95% ethanol.
- Absorbed oil must be removed by soxhlet extraction with a non-polar solvent, which may in turn cause additional extraction of components from the silicone, thereby skewing the results further from reality.

Silicone Elastomers - 3

- A proposed solution is to use Tenax which does not penetrate the silicone elastomer matrix.
- Tenax was an accepted substitute under Directive 97/48/EC but its use as a substitute under 10/2011, lacks clarity.
- Tenax also overestimates migration compared to normal bake ware (e.g. muffins, marble cake) but if the reduction factor of 5 is applied, the results are comparable to standard bake ware.

Silicone Elastomers - 4

- The most important criteria to determine suitability of silicone moulds for food contact is the limit for volatile substances (0.5%) as mandatory according to Recommendation XV of the BfR and the French legislation.
- In appropriately post-cured materials meeting the limit for volatiles <0.5% the majority of migrants consist of cyclic siloxanes with Mw >1000Da which according to present knowledge, are not expected to endanger human health.

Issues with 50% Ethanol

24

50% Ethanol - 1

- Some polyester based coatings show delamination and swell when tested under severe time/temperature conditions (e.g. 2 h 130 °C) with simulant D1 (50 % ethanol)
- The same polymeric coatings do not show any physical changes when they are in contact with milk products under equivalent sterilisation conditions.
- Overall migration tests and most specific migration tests cannot be carried out in milk products instead of simulants.

50% Ethanol - 2

- Proposal: Compliance of coatings which are not resistant to 50 % ethanol can be demonstrated by

  - decreasing testing time and/or temperature to a level where no physical changes of the coating film occur

  or

  - migration testing with simulant A (10 % ethanol) and D2 (vegetable oil) rather than 50 % ethanol

Relationship between simulant results and those in foodstuffs

27

Can Coating – example of food – 1

- A coating for metal packaging was needed for a range of foodstuffs with varying oily characteristics, from vegetables in oil to water/oil emulsions.
- Rather than use various simulants, including oil, 95% ethanol was used, as a worst case simulant to cover the range.
- 95% ethanol was an alternative to oil in Directive 97/48/EC, and although not in 10/2011, it is in revised Warenwet which would apply to coatings on rigid metal packaging.
- Customer also requested 95% ethanol.

28

Can Coating – example of food – 2

- The standard test protocol for 95% ethanol was 4 hrs @ 60º C (for sterilisation at 120 - 130º C), followed by 10 days at 40º C.
- Under the new conditions of 10/2011 and the Warenwet, the storage temperature is now 10 days @ 60º C, if these 'rules' are applied to non-plastics, which is common practice.
- Test results using 95% ethanol gave cause for further investigation.

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Can Coating – example of food – 3

- The results of extraction of a monomer into 95% ethanol, 10 days @ 60ºC, were compared to the levels in an aqueous / oily emulsion (D1 simulant in 10/2011) which was in packaging surrounded only by that coating.
- For comparison extraction into acetonitrile and hexane/acetone (1/1) (both 24 hrs @ ambient), gave values between 9 and 16 µg/6 dm^2.

30

Can Coating – example of food - 4

- The foodstuff was industrially processed and stored for 6 – 12+ months.
- 4 different batches of coating and packaging were used.
- The surface area to volume ratios (S/V) of the packaging was double the EU assumption of 1kg/6 dm^2 - given as corrected concentration using actual S/V ratios.

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Can Coating – example of food - 5

- Foodstuff industrially filled and processed < LOD of 70 µg/kg.
- Results of extraction into 95% ethanol.

package sample	storage conditions	conc. (µg/6 dm^2)	corrected conc. µg/kg
1	1 day at 60°C	105	210
	10 days at 60°C	370	740
2	1 day at 60°C	128	256
	10 days at 60°C	386	772
3	1 day at 60°C	133	266
	10 days at 60°C	394	788
4	1 day at 60°C	139	278
	10 days at 60°C	318	636

32

Can Coating – example of food - 6

- Clearly, the results in 95% ethanol are completely different to that in food.
- Whilst hydrolysis maybe occurring in 95% ethanol, it is not in the presence of the foodstuff.
- Reaching a conclusion about the safety of the coating using the extraction data would give rise to arguably unnecessary concerns about the safety of the coating.

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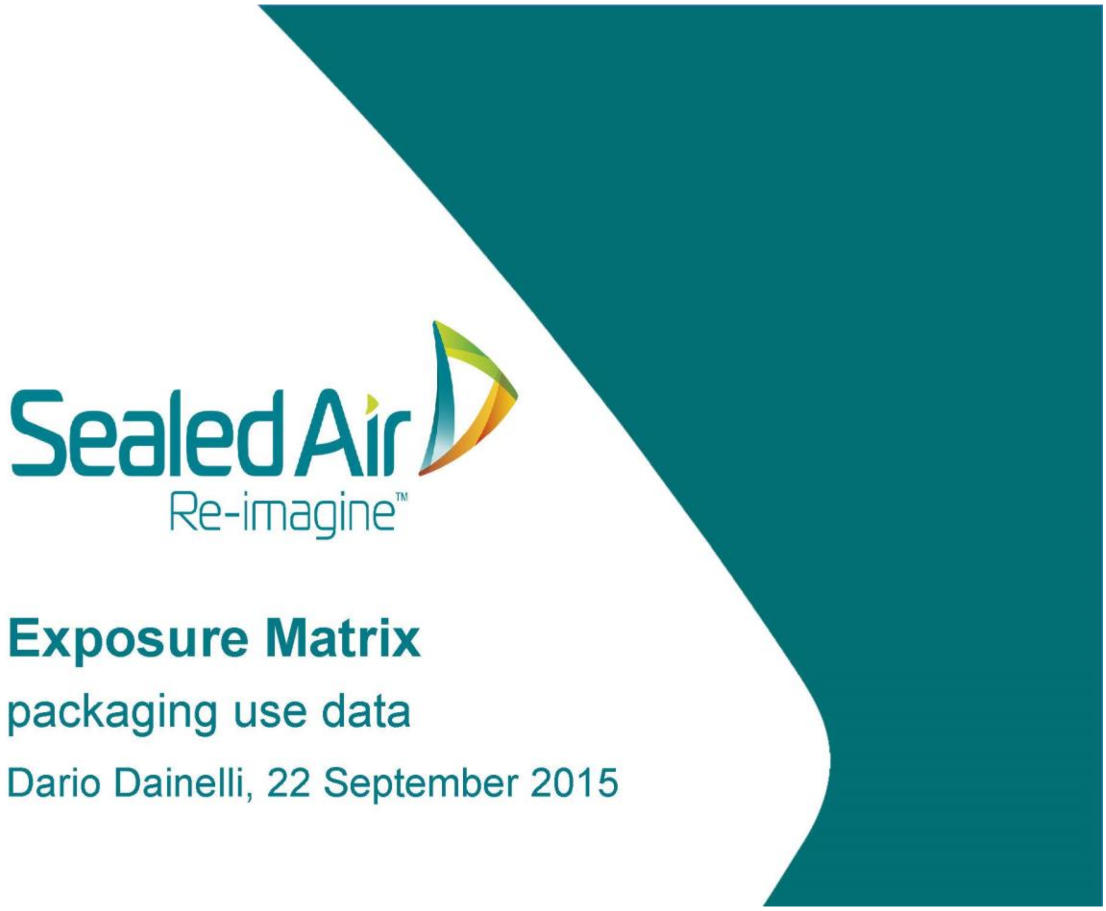
Acknowledgements

- All members of this task force for their inputs.
- In particular, for this presentation, Christa Burger, John Dixon, Beate Ganster, Catherine Simoneau, Richard Whitaker, Ulrich Nehring, Michelle Callow.

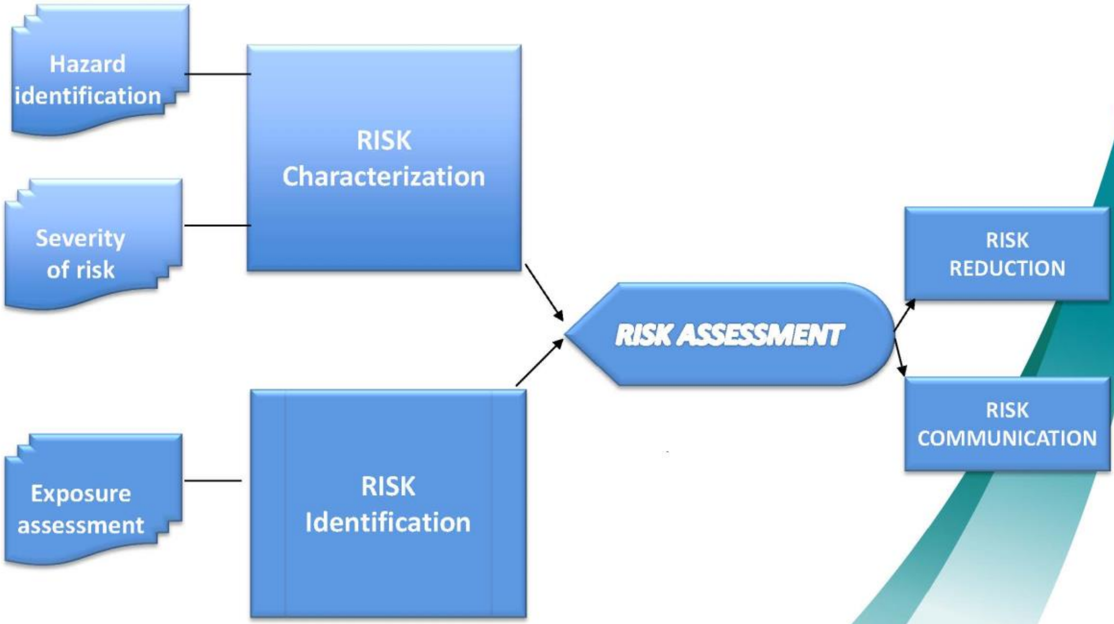
THANK YOU FOR YOUR ATTENTION

34

Matrix exposure tool for public use - Dario Dainelli, EUPC / Matrix group



Background



Industry Exposure Projects

Matrix:

- Now available on-line: www.matrixcalculation.eu
- Client-server, no need for downloading
- User friendly, trouble-free

FACET

What is www.matrixcalculation.eu ?

www.matrixcalculation.eu is a web-based tool for calculation of exposure to substances migrating from Food Contact Materials and Articles;

To be used in the exercise of Risk Assessment required by Article 19 of Reg. EU N0. 10/2011, in particular in relation to NIAS (Non Intentionally Added Substances) and NLS (Non-Listed Substances);

Represents a practical approach to enable risk management decided in a tiered way.

To be reminded:

Risk = Occurrence x Exposure

Exposure [µg/person/day] = Migration [µg/dm^2] x Surface [dm^2/person/day]

Surface distribution table

	Packaging mat.1	Packaging mat.2	Packaging mat. 3	Packaging mat. m
Food 1	D_{11}	D_{12}	D_{13}	D_{1m}
Food 2	D_{21}	D_{22}	D_{23}	D_{2m}
Food 3	D_{31}	D_{32}	D_{33}	D_{3m}
Food n	D_{n1}	D_{n2}	D_{n3}	D_{nm}

One more step

Tolerable Exposure Limit (TEL): if Exposure<TEL then Migration is trivial enough to avoid further assessment

Migration @ TEL= Level Of Interest (LOI), i.e. the level of migration below which no assessment is needed, but above which a risk assessment shall be done.

LOI [µg/dm^2] = TEL [µg/person/day] / S [dm^2/person/day]

May be set based on Cramer class, or may take other values depending on the level of risk that one wants to evaluate

Background of www.matrixcalculation.eu

The tools builds on the equation Exposure = Migration x Surface

The term “Migration” is either an experimental value or a calculated one (worst-case or migration modelling)

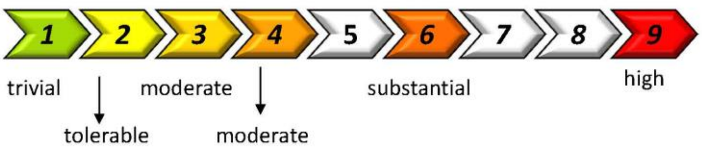
The term “Surface” represents the 50%ile of Packaging/Food D-curves, for 5 countries (FR, DE, IT, UK, ES).

Each Surface table (for each Country) consists of 51 food classes and 77 packaging materials

sub_basket	1 aluminium foil	2 paper	3 RCF (regenerated cellulose film)	4 Other mono-substrate plastic	5 Other monosubstrate non-plastic	6 VLDPE or LLDPE and blends with LDPE	7 LDPE	8 acid+ester copolymers (EVA, EMA, EAA, EBA)	9 other PE based blends	10 HDPE	11 multilayer PE	12 OPP	13 metallized OPP	14 other PP	15 PA	16 PC	17 PET (CPET and APET)	18 non-expanded PS	19 expanded PS (EPS)	20 plasticized (soft) PVC and PVDC	21 non-plasticized (rigid) PVC and PVDC	22 APET/PE	23 plastic/APET/PE	24 OPET/PE
01. Alcoholic Beverages	0	0	0	0	0.982	0	0		0	0	0	0	0	0			0.002	0	0	0	0	0		0
02. Non-alcoholic beverages	0.005	0	0	0	0.29	0	0.001		0	0.031	0	0	0	0.004			1.839	0	0	0	0	0		0
03. Concentrates of juices	0	0	0	0	0.009	0	0		0	0	0	0	0	0			0	0	0	0	0	0		0
04. Liquid coffee or tea	0	0	0	0.041	0.02	0	0		0	0.001	0	0	0	0			0.129	0	0	0	0	0		0
05. Dry beverage powders	0	0.133	0	0	0.017	0	0		0	0.008	0	0	0	0.09			0.012	0	0	0	0	0		0
06. Breakfast cereals and bars	0	0	0	0.067	0	0	0.002		0	0	0	0.007	0	0.001			0	0	0	0	0	0		0.019
07. Cereal flour	0	0.2	0	0	0	0	0		0	0	0	0	0	0			0	0	0	0	0	0		0
08. Dough	0	0.006	0	0	0	0	0		0	0	0	0	0	0			0	0	0	0	0	0.015		0.009
09. Bread	0	0.166	0	0	0	0.05	0.101		0.05	0.001	0.05	0.252	0	0.101			0	0	0	0	0	0		0.002
10. Dry rice and pasta	0	0.086	0	0	0	0	0.075		0	0.004	0	0.028	0	0			0	0	0	0	0	0		0.054
11. Fresh pasta	0	0	0	0	0	0	0		0	0	0	0	0	0			0.001	0.002	0	0	0	0.022		0
12. Sweet biscuits	0	0.114	0	0	0.003	0	0		0	0	0	0.179	0.091	0.012			0.069	0.001	0	0	0.006	0		0
13. Savoury/salty biscuits	0	0	0	0	0	0	0		0	0	0	0.032	0.003	0			0	0	0	0	0	0		0.005
14. Potato crisps and potato snacks	0	0.012	0	0	0	0	0		0	0	0	0	0	0			0	0	0	0	0	0		0
15. Roasted and/or salted nuts	0	0	0	0	0.005	0	0		0	0	0.001	0	0	0			0.001	0	0	0	0	0		0.011
16. Sugar	0	0.118	0	0	0	0	0.002		0	0	0	0	0	0			0	0	0	0	0	0		0
17. Sugar confectionery	0	0.005	0.004	0.001	0	0	0		0	0	0	0.005	0.001	0.005			0	0	0	0.001	0	0		0.001

Proposed model for Risk Assessment

Risk characterization					
Very harmful	3	3	6	9
Harmful	2	2	4	6
No or slightly harmful	1	1	2	3
		1	2	3
		Low	Medium	High
		Risk identification		



Steps for exposure assessment and risk assessment on a FCM

1. Decide conditions and simulant(s)
2. Migration test / analysis ➔ chromatogram
3. ALTERNATIVELY: determine worst-case migration
4. Option: determine a LOI
5. Identify the substances for which Exposure needs to be calculated (exclude those in positive list, optionally exclude those below LOI)
6. Run www.matrixcalculation.eu and determine exposure
7. Use exposure in a Risk Assessment exercise

Deep dive into Matrix

- Overview
- Definition of food groups.
- Packaging description.
- Surface/volume ratio.
- Packaging use data for Germany.
- Packaging use data for UK, France, Italy, Spain.

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Overview

- packaging use data for **DE, UK, FR, IT, ES** = 300 mio consumers
- intention to cover the entire diet (excluding dietary supplements)
- packaging use: consumer retail market
  → primary packaging, pre-packed foods
  - excludes over-the-counter sales and vending
  - DE: data purchased from the *Gesellschaft für Verpackungs-Marktforschung* (GVM)
  - UK/FR/IT/ES: data purchased from *EuroMonitor* (EM)
- covers all packaging materials, but most refined only for plastics

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Definition of food groups

- 51 food groups
  - starting point = Re. 10/2011
  - some modifications to better reflect different packaging technologies used
    e.g. distinction dry / liquid / refrigerated / frozen / preserve.
- GVM and EM in-house data uses their own food descriptions
  - these were mapped against the 51 food groups defined
  - some differences between GVM and EM mapping
  - document on mapping individual food items against in-house food groups is available from both institutes

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1. alcoholic beverages including wines, beers and liquors	27. frozen fruits or frozen fruit pastes
2. non-alcoholic non-dairy beverages including waters, juices and soft drinks	28. fresh fish and seafood
3. concentrates of juices and soft drinks; syrups for dilution	29. processed fish and seafood products, excluding preserves and frozen
4. liquid coffee or tea preparations	30. fresh meat including poultry and game; fresh raw sausage
5. dry coffee, tea, cocoa powder, dry beverage powders	31. processed meat products, excluding preserves and frozen
6. cereals; cereal flakes or bars; breakfast cereals and muesli; pop-corn; seeds	32. preserves of fish, seafood, meat or preserves of processed fish, seafood, meat products
7. cereal flour and meal (including self-raising), starches	33. frozen meat, fish or seafood, unprocessed (frozen processed are in 47)
8. dough	34. eggs and processed (liquid, powdered or dried) egg fractions
9. bread including pizza bottoms, blinis, toasted bread etc.	35. liquid milk, flavoured milk drinks, milk concentrate, cream
10. dry rice and pasta without seasoning, including plain dried noodles	36. dried milk powder
11. fresh (uncooked) refrigerated pasta without seasoning	37. dairy products and preparations with or without fruit (fromage frais is in 38)
12. sweet biscuits, cakes, pancakes, pastry, including chocolate-coated	38. cheese
13. savoury/salty biscuits, crackers, crispbreads	39. ice-cream and frozen yoghurt
14. potato crisps, potato snacks, tortilla chips	40. fats and oils of animal or vegetable origin, including butter and margarine
15. roasted and/or salted nuts, and snack mixtures mainly composed of these	41. liquid oily sauces (mayonnaise, vinaigrette, salad dressings etc.)
16. sugar	42. liquid non-oily sauces (soy based sauces, pasta sauces, liquid stocks, etc.)
17. sugar confectionery	43. liquid soups (frozen are in group 47)
18. sugar-based syrups not for dilution; honey	44. herbs, spices, salt; powders for soups, sauces and desserts; stock cubes
19. chocolate spreads and syrups; peanut butter	45. vinegar, mustard, ketchup and other condiments
20. chocolate and chocolate confectionery	46. yeast and raising agents
21. fresh vegetables, green salads and lettuce, potatoes	47. prepared meals and meal components, frozen
22. vegetable preserves	48. prepared meals and meal components, refrigerated
23. frozen vegetables	49. prepared meals and meal components, dehydrated, including dried potato, vegetable
24. fresh fruit, whole or cut	50. prepared meals and meal components, preserves
25. dried fruit, nuts (excluding roasted and salted nuts), and mixtures of the two	51. infant formula and baby food
26. fruit preserves	

Definition of food groups

- GVM data
  - 348 in-house subsectors
  - these were aggregated to 62 subsectors
  - data reported in 51 sectors with 62 subsectors
- EM data
  - 156 in-house subsectors
  - data reported in 51 sectors with 156 subsectors

COUNTRY	SECTOR	SUBSECTOR
	Beverages	Bier
		Wine
		Fruit Juice
		…

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Packaging description

A. Mono-substrate packaging materials

1. aluminium foil
2. paper
3. RCF (regenerated cellulose film)
4. other mono-substrate
   4.1. other mono-substrate plastic
   4.2. other mono-substrate non-plastic
5. monolayer PE
   5.1. VLDPE or LLDPE and blends with LDPE
   5.2. LDPE (density> 0.9)
   5.3. Acid + ester copolymers (EVA, EMA, EAA, EBA)
   5.4. HDPE
   5.5. Other PE based blends
6. multilayer PE
7. Polypropylene
   7.1. OPP
   7.2. metallized OPP
   7.3. other PP
8. PA
9. PC
10. PET (CPET & APET)
11. PS
    11.1. non-expanded PS
    11.2. EPS
12. PVC (& PVDC)
    12.1. plasticized (soft)
    12.2. non-plasticized (rigid)

B. Multi-substrate plastic packaging materials

13. APET/PE *or* plastic/APET/PE
    OPET/PE *or* plastic/OPET/PE
    metallized-OPET/PE *or* plastic/metallized-OPET/PE
14. PVC/PE *or* plastic/PVC/PE
15. PA/PE *or* plastic/PA/PE
    OPA/PE *or* plastic/OPA/PE
    metallized-OPA/PE *or* plastic/metallized-OPA/PE
16. OPP/PE *or* plastic/OPP/PE
    PP/PE *or* plastic/other polyolefin/PE
17. other plastic/PE
18. OPP/OPP *or* plastic/OPP
    OPP/metallized-OPP *or* plastic/metallized-OPP
    PE/PP *or* other plastic/PE/PP
    other plastic/PP
19. plastic/PET
20. PE/ionomer
    other plastic/ionomer
21. other plastic/other plastic

C. Multi-substrate multi-material flexible packaging materials

22. aluminium/paper *or* aluminium/plastic/paper
    plastic/aluminium/paper *or* plastic/aluminium/plastic/paper
23. aluminium/paper/plastic *or* aluminium/plastic/paper/plastic
    plastic/aluminium/paper/plastic *or* plastic/aluminium/plastic/paper/plastic
24. aluminium/PE *or* aluminium/plastic/PE
    plastic/aluminium/PE *or* plastic/aluminium/plastic/PE
25. aluminium/plastic (non-PE) *or* plastic/aluminium/plastic (non-PE)
26. paper/aluminium/plastic *or* paper/plastic/aluminium/plastic
    plastic/paper/aluminium/plastic *or* plastic/paper/plastic/aluminium/plastic
27. plastic/aluminium
    paper/aluminium *or* paper/plastic/aluminium
    plastic/paper/aluminium *or* plastic/paper/plastic/aluminium
28. paper/plastic *or* plastic/paper/plastic
29. other combination of non-plastic(s) and plastic(s)

Packaging description

- food contact side is to the right
- classification based on "substrate" e.g. a film
  the substrate itself may be mono-layer or multi-layer (co-extrusion).
- no split according to presence/absence of inks /coatings / adhesives.
- polymer types are generic unless otherwise indicated, for example:
  - in group 5 the "PE" is split according to copolymers;
  - in groups 6, 13-29 "PE" includes blends, co-extrusions and copolymers;
  - use of "other PE", "other PP", "other plastic".

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Packaging description

- 29 material groups defined with 77 subgroups
  - GVM and EM generated new data i.e. the split of their in-house data according to the required packaging descriptions
  - EM data reported at subgroup level
  - GVM data reporting
    - groups / subgroups maintained for plastics
    - 8 groups / 26 subgroups defined for plastic/non-plastic multilayers were aggregated back to 4 groups
    - 4 groups defined for non-plastic materials were aggregated back to 2 groups

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Packaging description

- Multi-component packaging e.g. tray with lid, bottle with cap:
  - GVM distinguishes between
    - main pack
    - caps or other side materials
  - EM distinguishes between
    - main pack
    - side material (e.g. a lidding film on a tray)
    - cap (e.g. on a bottle or jar)
    - separator (e.g. insert between slides of ham)
  - EM data includes in-house classification of pack types.

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I. Metal
1. Metal food can
2. Metal beverage can
3. Metal aerosol can
4. Metal tins
5. Aluminium container/tray
6. Collapsible metal tubes
7. Other metal
8. Kegs

II. Rigid plastic
1. Rigid plastic PET bottles
2. Rigid plastic HDPE bottles
3. Other plastic bottles
4. Rigid plastic jars
5. Other rigid plastic containers
6. Thin wall plastic containers
7. Rigid speciality cosmetics containers
8. Squeezable plastic tubes
9. Plastic trays
   9.a. Ready meal trays
   9.b. Other plastic trays

III. Glass
1. Glass bottles
2. Glass jars

IV. Liquid cartons
1. Gable-top liquid carton
2. Brick-shape liquid carton
3. Other shaped liquid cartons

V. Paper-based containers
1. Folding cartons
2. Composite containers/ tubes
3. Board tubs
4. Bag-in-box

VI. Flexible packaging
1. Stand-up pouches
   1.a. Plastic pouches
   1.b. Aluminium/plastic pouches
2. Flexible plastic
3. Aluminium foil
4. Flexible paper
5. Flexible aluminium/plastic
6. Flexible aluminium/paper
7. Flexible paper/plastic
8. Blister and strip packs

VII. Other packaging

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Surface/volume ratio

- GVM in-house data includes S/V ratio from sample purchases
  - surface / food volume for most rigid packaging
  - surface / food weight for most flexible packaging
  - aggregated S/V calculated by most-frequent-value method
  - packaging area calculated from aggregated quantity of food packed and aggregated S/V

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Surface/volume ratio

- EM in-house data does not include S/V ratio
  - primary data reported includes pack size (i.e. food content) and number of packs per pack size
  - we proposed a theoretical model to calculate S/V ratio based on pack size and on three geometric shapes:
    - "brick" shape, with 10% headspace
    - "bar" shape, with 25% headspace
    - "flat" shape with a volume-dependent 'aspect ratio' and with 50% headspace
  - EM assigned pack shape and calculated S/V and packaging area at the individual pack item level (*note: discuss bundle wrap*)

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GVM packaging use data for DE

- primary in-house data from 2003
- data reported for 61 food descriptions against 54 packaging descriptions, each data point split between main/side
- types of data reported:
  - volume of food at aggregated food group level
  - surface/volume ratio
  - calculated packaging area
  - split between rigid and flexible packaging

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EM packaging use data for UK/FR/IT/ES

- primary in-house data from 2005
- data reported for 156 food descriptions against 77 packaging descriptions
  - each data point split between main/side
  - additionally split per EM pack type
  - additionally split per pack size
  - → **8000 lines of data**
- types of data reported:
  - number of sales units for each pack size
  - volume of food for each pack size
  - calculated S/V ratio and packaging area

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Conclusions

Access to raw data available if requested

Possible trainings if needed, organized by Associations

Presentation to DG Santé not done yet, but proposed

Already used by industry

Recommended to use to all stakeholders, including Control labs.

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Back-up

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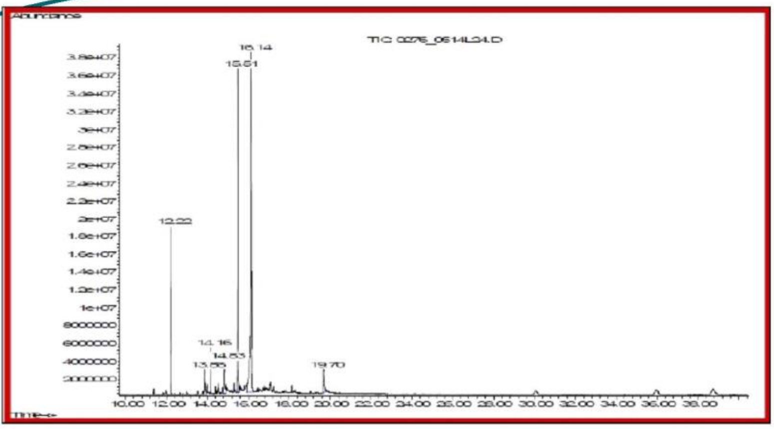
OPP monolayer



TR	peak identification	qual	SEMIQUANTITATIVE EVALUATION µg/dm²
12.22	BHT	98	45
13.86	Cyclohexadecane	91	11
14.16	**Di propyl phthalate (internal standard)**	**94**	**12,5**
14.83	7,9-Di-tert-butyl-1-oxaspiro(4,5)deca-6,9-diene-2,8-dione	98	13
15.51	Sebacic acid, dibutyl ester	91	84
16.14	Tributyl acetylcitrate	91	145
19.70	Erucamide	87	15

Identify the substances in positive list

- BHT (#315) : has an SML : 3 mg/kg, conc : 45 µg/dm² => 45x6 µg/kg* => 0,27 mg/kg
- Sebacic acid dibutylester (#242) & tributyl acetyl citrate (#138), group SML (32) : 60 mg/kg => 84 + 145 µg/dm² = 229 µg/dm² => 229x6 µg/kg = 1,37 mg/kg
- Erucamide (#271) : has no SML (permitted additive to plastics used in food packaging) => max allowed migration: 60 mg/kg (art 11.2 of 10/2011) =>15µg/dm² => 0,09 mg/kg

Substances to be further assessed:
Cyclohexadecane (CAS 295-65-8),
7,9-di-tert-butyl-1-oxaspiro(4,5)deca-6,9-diene-2,8-dione (CAS 82304-66-3)

1. Use of QSAR to determine the Cramer Class:
   1. Cyclohexadecane (CAS 295-65-8) : Cramer class I – TTC of 1800 µg/person.day
   2. 7,9-di-tert-butyl-1-oxaspiro(4,5)deca-6,9-diene-2,8-dione (CAS 82304-66-3): Cramer class III - TTC of 90 µg/person.day
2. Use of www.matrixcalculation.eu to calculate exposure and benchmark with TTC (EXAMPLE)

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4. List of participants

EUROPEAN COMMISSION
JOINT RESEARCH CENTRE

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